FIELD STUDY TO ASSESS THE FEASIBILITY OF DISPOSING OF DIESEL INVERT-BASED CUTTINGS RESIDUES USING LAND APPLICATION

for

Environmental Research Advisory Council

Canadian Petroleum Association

and

Conservation and Protection

Environment Canada

J. Ashworth

Norwest Soil Research Ltd.

Edmonton, Alberta

August 1990

Funding for this research was provided by the Environmental Research Advisory Council (ERAC) of the CPA and the Federal Panel for Energy Research and Development (PERD)

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92-02805/

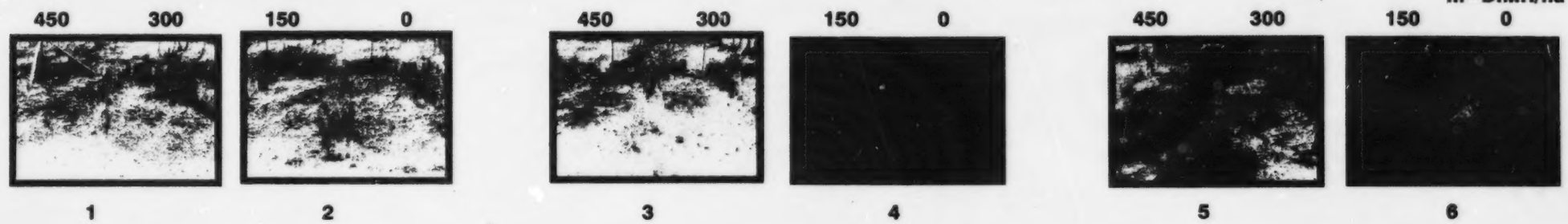
Grass Growth in 1987, 1988 and 1989 Following DIMR Application in June 1986

North Section (Cultivated)
Front half of plots manured.

Centre Section (Uncultivated)
Front half of plots manured.

South Section (Uncultivated)
Charcoal (front). Carbon (back).

m^3 DIMR/ha



EXECUTIVE SUMMARY

"Invert" drilling fluids consist of a dominant organic liquid component in which inorganic additives are dispersed, unlike conventional fluids which are water-based and mainly inorganic in composition. When sections of oil or natural gas wells are drilled with diesel oil-based invert mud, a residue of diesel invert mud and rock cuttings (referred to below as DIMR) is produced. In addition to the oil component, DIMR often contains heavy loadings of added salts such as calcium chloride.

The use of invert muds to facilitate drilling operations has become widespread in Alberta in recent years. Although quantities of DIMR vary with both well depth and efficiency of residue recovery, several hundred cubic metres is a typical volume for sour gas wells drilled in the Alberta foothills.

The safe disposal of DIMR has become an issue of concern to environmentalists as well as to producers of energy. Disposal options include incineration and solidification but technical problems have arisen with both these approaches. To industry, the most cost-effective option would be "land treatment" in which DIMR is spread over the lease and worked into the soil.

However, difficulties in reclaiming sites used for land disposal of DIMR (and regulatory considerations regarding land treatment generally) have caused misgivings over using this disposal option. Concerns have been expressed that organic constituents of DIMR, which include many polyaromatic hydrocarbons (PAHs) might (i) take too long to degrade in soil (ii) prevent growth (iii) be taken up by plants and harm grazing animals or (iv) leach into the subsoil and groundwater.

To test and demonstrate the land treatment option, DIMR was rototilled into the surface soil of small plots in June 1986 and various soil amendments including manure, fertilizer, charcoal and spent carbon-granules employed before seeding with a mixture of grasses. Most of these amendments had previously been tested in laboratory work.

Due to the calcium chloride component of the DIMR used, all treated plots were so saline that no revegetation treatment was effective in the season of application (Plates 1-6)*. However, the salts were mostly leached away by good summer rainfall in 1986 and 1987, and oil degradation was rapid on fertilized plots, especially those given a surface mulch of manure. These mulched plots were largely revegetated by fall 1987 and completely by fall 1988 (Plates 9, 10, 15, 16, 19, 20 & 21). Plots which were fertilized and cultivated required an extra season for complete revegetation when treated with 300 or 450 m^3/ha of DIMR (Plates 7, 8, 13 & 14).

Fertilization alone, without either manure or cultivation was not a successful strategy for revegetation (Plates 22 & 23). On areas given no

*Plates 1-6, 7-12 & 13-18 (taken June '87, July '88 & Aug. '89 respectively) show pairs of plots from each section of the field trial (see Fig.1). There is a 3' guard strip between plots. DIMR rates (l. to r.) in each section were 450, 300, 150 & 0 cu.m/ha. Plates 19-23 show individual plots.

Centre Section (Uncultivated). Front half of plots manured.

450 m^3 of DIMR/ha

1987 | 1988 | 1989

N ← N ←

19 | 20 | 21

Fertilized (front) and Unfertilized (middle) strips. Back half of plot (looking west) manured.

Centre Section Uncultivated — 1989

North Section Cultivated — 1989

Centre strip unfertilized — No Manure ← 1989 → Manure

→ N

22 | 23 | 24

Looking South from N end of site

fertilizer, there was some oil degradation but little or no growth (Plates 22, 23 & 24) up to the fall of 1989. The charcoal and carbon-granule treatments (in contrast to lab findings) were detrimental to growth and may have slowed oil degradation (Plates 11, 12, 17 and 18).

Target PAHs had half-lives of only a few months in soil, even on unfertilized plots. All hydrocarbons were retained near the surface and there was very little leaching. No target compounds were detected in soil 30 cm below the surface. Only background concentrations of target PAHs were found in healthy plants on plots where revegetation was successful.

The soil at the experimental site was slow draining and low in organic matter, consequently far from ideal as a medium for receiving salty, oily waste. Also, soil temperature would not have been favourable to degradation because the site was at high elevation. Therefore, more field work is needed at other sites, but the results from this site suggest that land treatment is a practical and environmentally acceptable means of disposal of DIMR, provided that (a) rates of application are not excessive - incorporating a 3 cm depth, which is 300 m^3 per hectare, of DIMR with 10-15% oil appears to be a suitable rate - and (b) the level of site management needed for successful revegetation and safe degradation of hydrocarbons can be sustained for several seasons. Without intensive site-management (manure mulching and/or repeated cultivation, plus repeated fertilization) land treated with DIMR will remain oily and infertile for many years.

The results of this study also indicated that the target PAHs monitored in DIMR did not exacerbate problems with site revegetation and that these PAHs were neither taken up by plants nor leached into subsoil in significant quantity. Leaching and uptake of PAHs is to be expected only on coarse-textured soils very low in organic matter; these are uncommon in the Rocky Mountain foothills.

Basic reclamation treatment for DIMR-treated land (salt removal, heavy nitrogen fertilization and cultivation) is similar to that required for areas accidentally contaminated with oil and brine. There have been numerous such spills in Alberta and sites are known to respond well to intensive management along these lines.

Recycling of invert fluid from the cuttings, in addition to its economic benefits, has the advantage of minimising the hydrocarbon residue in the treated soil. Clearly, DIMR land treatment should not be carried out near surface water or known sources of potable groundwater. Also, run-off from the treated area should be prevented by ensuring that treatments are done on level ground or within dyked areas.

Desirable soil properties for DIMR land treatment include (i) adequate permeability so that salts in the DIMR can leach and disperse reasonably quickly, (ii) adequate organic matter content so that the risk of hydrocarbon leaching is minimal and (iii) good microbiological activity to facilitate oil degradation. For all these reasons, topsoil stripping without replacement is undesirable.

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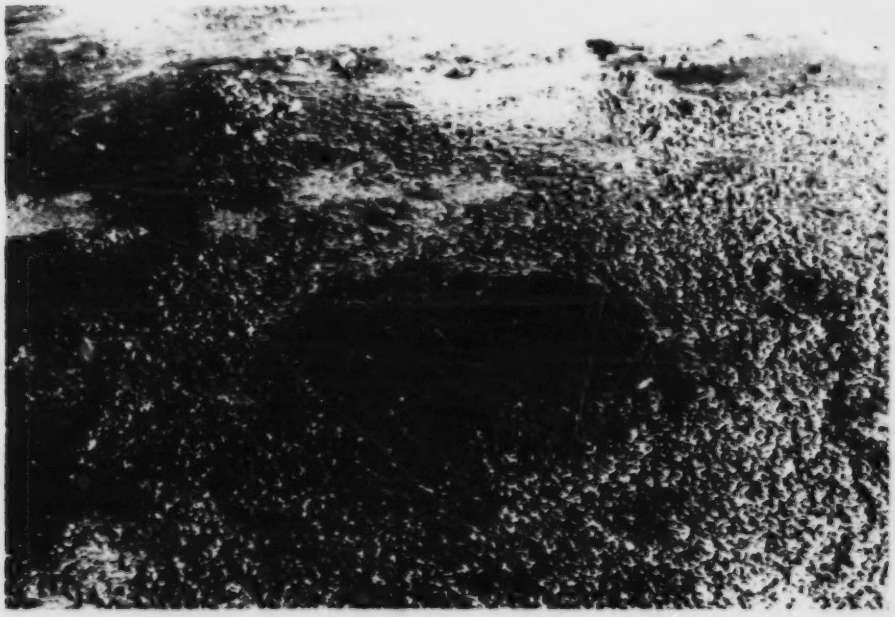


1. INTRODUCTION

1.1 Background

DIMR is the semi-solid residue left after oil or gas wells have been drilled using diesel-based "invert" mud, in which the dominant liquid component is diesel oil (see Plate 25). In addition to the vast range of hydrocarbons typical of most types of oil, the DIMR usually contains inorganic salts including calcium and sodium chlorides, as well as rock cuttings. The typical appearance of DIMR is shown in Plate 26.

Concern regarding land application of hazardous wastes in general, and problems with reclaiming sites used for disposal of DIMR in particular, led to recognition of a need to investigate land-disposal of DIMR.

The Environmental Research Advisory Committee (ERAC) of the Canadian Petroleum Association (CPA) and the Conservation and Protection Service (C&P) of Environment Canada funded a 2-year laboratory and greenhouse study (Peake et al., 1986) and the field study which is the subject of this report, with the objective of assessing the feasibility of land application of invert DIMR.

This work was desirable because the use of diesel invert muds in drilling has greatly increased in recent years. Although quantities of DIMR vary with both well depth and efficiency of residue recovery, several hundred cubic metres of DIMR must normally be dealt with during drilling-lease restoration. Incineration or solidification disposal options are uneconomic and technically difficult; however, disposing of the residue on the lease presents environmental problems because of the well-known inability of plants to grow on soil that is badly contaminated with oil (Plice, 1948) and because toxic and potentially refractory PAHs are present in diesel oil.

1.2 Laboratory and Greenhouse work

This work has been reported by Peake et al., 1986. To summarize it briefly; DIMR samples from two sour gas well sites near Bragg Creek (in the Rocky Mountain foothills, near Calgary) with approximately 1% aromatic hydrocarbon content (about 11% total hydrocarbon content) were mixed (at rates up to 40 g per 100 g of soil) with topsoil taken from near the two sites. Degradation in aerated columns of moist soil at 23°C was monitored by passing effluent air through a carbon dioxide trap and by extracting residual hydrocarbons from the soil. Up to 63% of aliphatic and aromatic hydrocarbons in 30% DIMR/soil mixtures had disappeared after 8 months, the rate being dependent on soil type and the amount of nitrogen fertilizer applied. However, aromatic compounds of high molecular weight (m/e 192 and above) showed little or no loss. The disappearance of lower M.W. aromatics was tentatively ascribed to their volatility.

Germination and growth of grasses in pots of treated soil was strongly inhibited by DIMR but had returned almost to normal 5 weeks after DIMR treatment. Alfalfa was more sensitive and did not develop past the cotyledon stage until at least 14 weeks after DIMR application.

Growth was greatly improved when activated charcoal was applied at heavy rates to the DIMR/soil mixtures. Spent carbon granules (from filters which purify monoethanolamine used to refine natural gas) also improved growth in these greenhouse trials.

2. FIELD DEMONSTRATION

2.1 Materials and Methods

The DIMR used in the field experiment was obtained from a newly completed well (courtesy of Home Oil Ltd.). The DIMR was well mixed by backhoe in a small pit adjacent to the experimental site. Six representative samples taken by auger from the centre of the DIMR contained on the average 11.4% hydrocarbons on an as-received basis. Over 90% of the hydrocarbons were non-aromatic, about 6% were aromatic and 1% were polar compounds. This DIMR was therefore similar to the Quirk Creek DIMR used in the greenhouse work of Peake et al. (1986). In preliminary analytical work, five groups of PAHs, namely naphthalenes, phenanthrenes, biphenyls, fluorenes and dibenzothiophenes were detected and chosen as target compounds. No benzo(a)pyrene or target heterocyclic compounds were detected (see Appendix).

Leachate and acid digest analyses showed that the DIMR contained no abnormally high concentrations of heavy metals (see Appendix).

Salinity measurements showed that the DIMR had a very high electrical conductivity (EC) of 80 dS/m due to 600 mEq of calcium chloride and 200 mEq of sodium chloride per litre of the extract from a saturated paste.

Activated charcoal (Hydrodarco B) was supplied by Van Waters & Rogers Ltd. Spent carbon granules, used in filters as an absorbent in a monoethanolamine sour-gas refining process, were supplied by Alberta Gas Ethylene Ltd. (courtesy D. Wurster, Joffre plant).

2.2 Field site and treatments

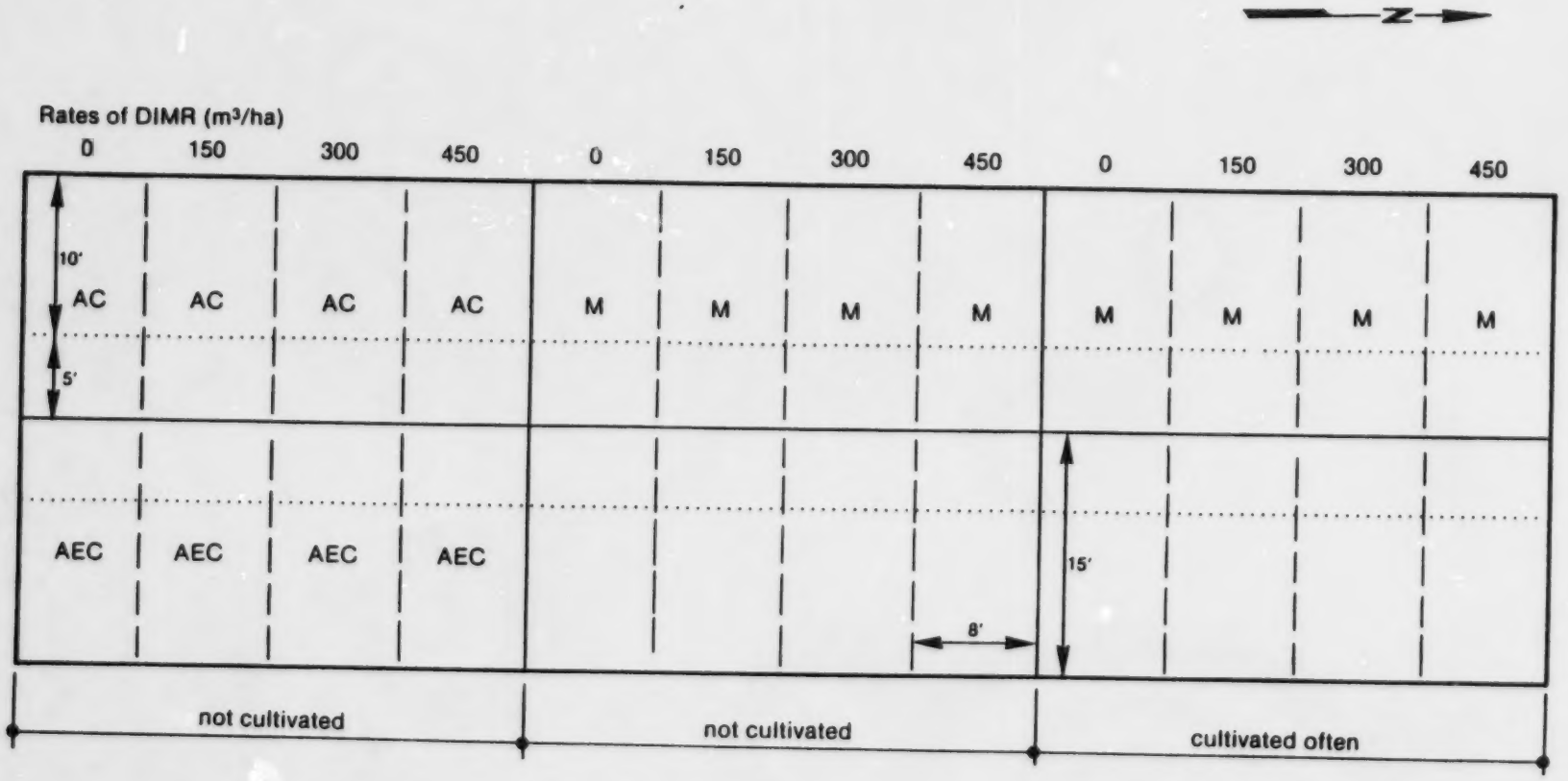
The experimental site was a cleared area (previously aspen woodland) gently sloping to the south-west, at an elevation of about 1500 m in the Rocky Mountain foothills (Plate 27). The soil was a clay loam, low in N and P, with pH 7.5 and 4% organic matter.

2.2.1 Field Work in 1986

The DIMR was spread and incorporated using a combination front-end loader/rototiller on plots measuring 9.1 x 2.4 m at 150, 300 or

27 General View of Area surrounding Site of Field Demonstration (Fenced Area between Truck and Trees)

Fig. 1. Layout of field experiment.
AC - activated charcoal AEC - Alberta Ethylene Carbon
M - manure (these treatments applied to an area 15' x 8')
The 10' wide central strip received no fertilizer.



450 m^3 per hectare (1.5, 3.0 or 4.5 cm layer). These rates straddle the anticipated rate required to dispose of a typical volume of DIMR within a 1 ha lease. Three replicate plots were prepared at each rate of DIMR, starting at the lowest rate and working up. There were also three control plots. A 3' wide strip (not shown in Fig. 1) separated each of the treatments.

The following amendments (see Fig. 1) were applied to half-plots on June 3, 1986: activated charcoal, incorporated by rototiller at 25 t/ha; spent carbon granules, incorporated at 10 t/ha; well-rotted manure at 45 t/ha, either incorporated (north plots) or left on the soil surface as a mulch (centre plots); no amendment. The amounts of each amendment were decided on the basis of availability and cost. Fertilizer supplying 240 kg N, 44 kg P, 41 kg K and 18 kg S /ha (rates used were based on soil-test results) was broadcast on part of the area occupied by these treatments; a central dividing strip was left unfertilized. The site was sown to a mixture of grasses plus oats (84 kg of seed mix/ha) one week afterwards. The seed mixture consisted of equal weights of perennial ryegrass, creeping red fescue, slender wheatgrass and oats.

The original intention had been to cultivate the north set of plots often, in order to test the effect of frequent aeration and disturbance on the rate of oil degradation. However, due to heavy rain throughout the summer of 1986, the first cultivation was not done until the end of September.

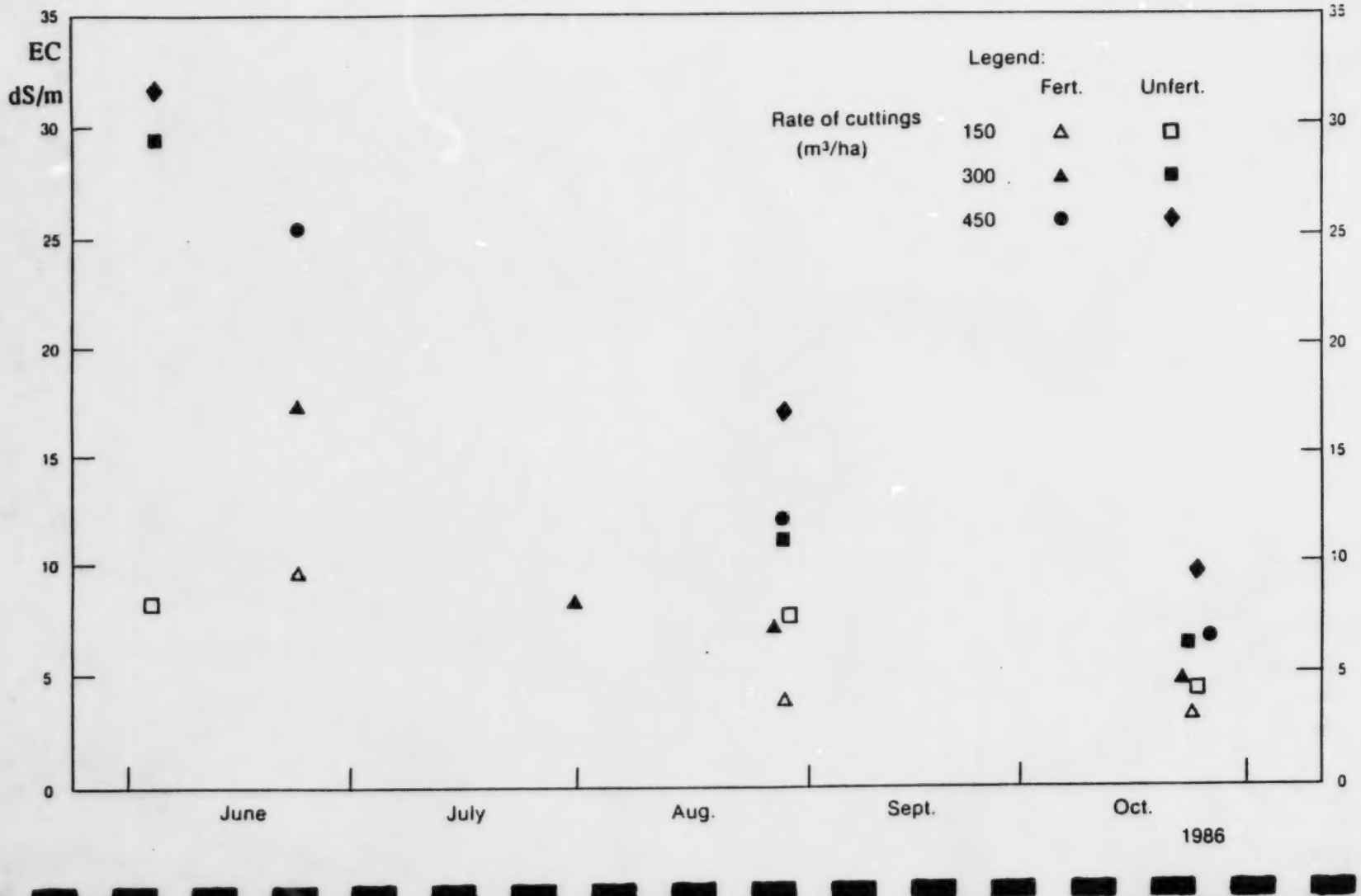
Then in October 1986, because of the general failure of seedling establishment on treated plots, the entire site was rototilled and 210 kg N/ha broadcast except on the central strip. Manure was again applied to the appropriate half-plots at 40 t/ha and either cultivated in or left as a mulch. A new mixture of grasses plus winter wheat was broadcast. This seed mixture consisted of perennial ryegrass, creeping red fescue, alkali grass, tall wheat grass and winter wheat.

2.2.2 Field Work in 1987

In June 1987 the north plots were rototilled again; 210 kg N/ha and 37 kg P/ha were applied except to the central strip. The same seed mixture as in October 1986 but mixed 50/50 with timothy seed was broadcast and lightly raked in over the entire area. Timothy was chosen because volunteer timothy had appeared in late summer 1986. However, at that time there was virtually no growth on any of the treated plots except for slight growth at the 150 m^3/ha rate of DIMR on the manure-mulched plots.

Nitrogen was again applied at 210 kg/ha in August 1987 and "Glean" herbicide sprayed over the entire site to suppress small areas of broad-leaved vegetation. "Glean" is a selective broad-leaf herbicide and did not affect growth of grasses. Plots with significant growth were harvested (1.5 sq.m) in October 1987 using shears. After harvest the entire site was razed with a "weed-whipper" and raked clear for the next season's growth. This treatment ensures that the entire plot is treated in the same way as the small, harvested patch. Except for the manure mulched area, where

Fig. 2. Electrical Conductivity of DIMR-treated soil during 1986 growing season



growth was becoming well established, growth was poor. All plots, therefore, except those with the manure mulch were then again roto-tilled and the site was seeded again as in June 1987.

2.2.3 Field Work in 1988

In September the site and surrounds were again sprayed with "Glean". In October the plots were again harvested as in October 1987.

In November 1988 the site was razed and cleared as before. Fertilizer was broadcast except on the central strip, to supply 210 kg N, 37 kg P, 27 kg K and 11 kg S/ha.

2.2.4 Field Work in 1989

In October selected plots were again harvested as in previous years.

2.3 Soil Sampling

Soil samples were taken (8 cm diameter auger) from approximately the top 10 cm from the north set of plots immediately after DIMR application. On four subsequent occasions each year (1986-1988), sets of samples were taken using a smaller sampler (core diameter 3 cm). On these occasions up to 12 cores were taken to 10 cm depth, the cores combined and a representative sample (often the entire sample) tied in a plastic bag for subsequent analysis. Sampling below 10 cm was badly hampered by small rocks. (Plates 22 and 27 give a good indication of the number of rocks at the soil surface). Where possible, cores were retrieved and combined but the objective of 12 cores was impractical and most sub-samples consisted of 4-5 cores only. The middle rate of DIMR application (300 m^3/ha) was sampled on more occasions than the other rates.

In October 1988, subsoil samples were taken from three plots by first excavating a small trench to about 25 cm, then augering the subsoil. This method avoided contaminating the subsoil with surface material. Plots given 450 m^3/ha of DIMR either alone, or plus carbon granules, or plus manure mulch and fertilizer, were sampled. The trench was dug mid-way along the plots, 15 cm in from the edge.

In 1989, soil samples (0-10 cm) were taken in October to assess the extent of oil degradation on plots given the top rate of DIMR.

2.4 Analytical Methods

2.4.1 Soil samples

Soil analysis for pH, EC, major cations and anions, and SAR was done on the filtrate from a saturated paste of the soil sample and water. Hydrocarbon content ("% oil") was measured by methylene chloride extraction of air dried and ground samples except in 1988 and 1989 when moist samples were extracted with toluene in a Soxhlet apparatus with a Dean-Stark trap to remove water. This method avoids volatilisation losses on air-drying.

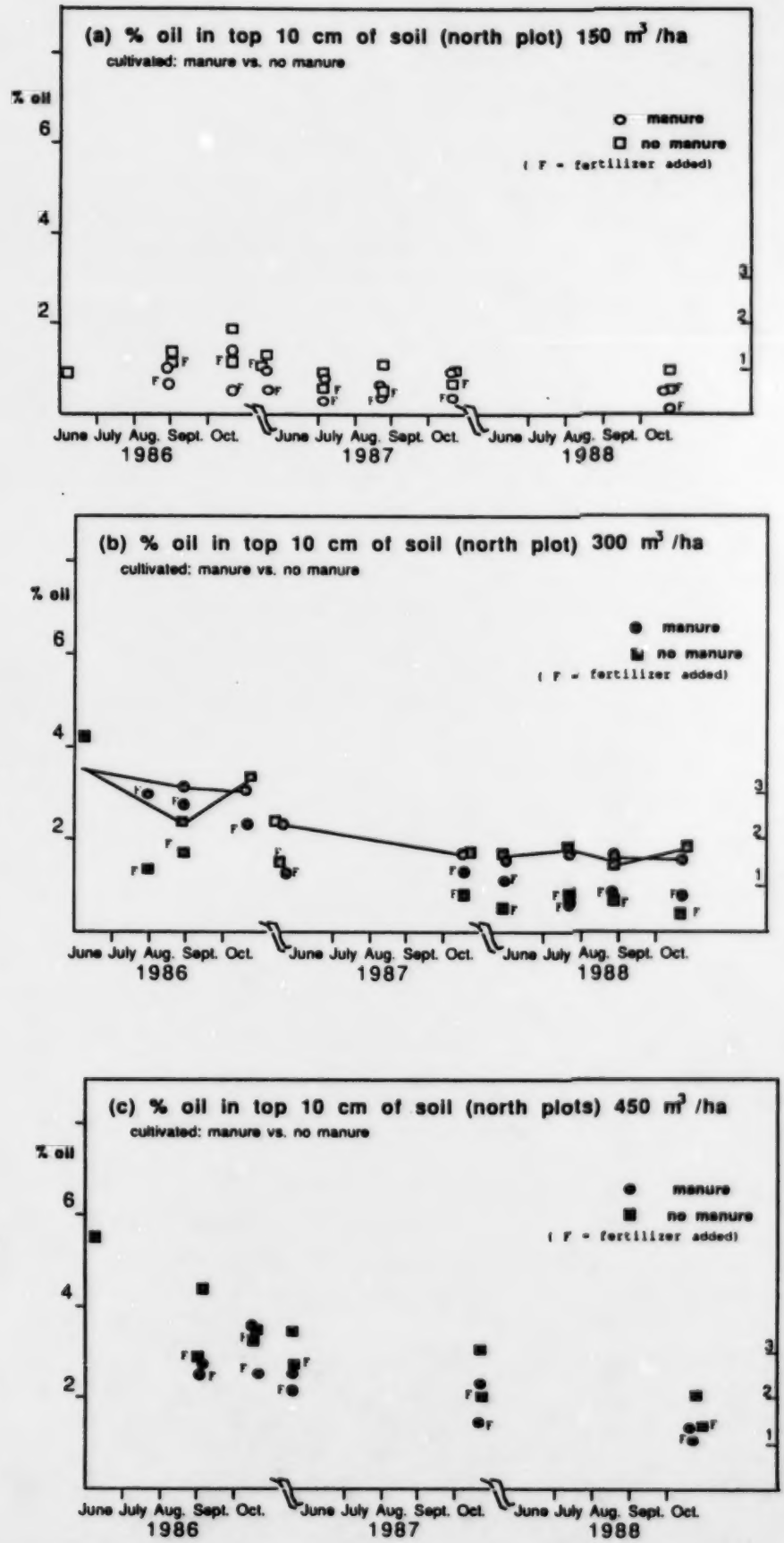


Fig. 3. Oil content of DIMR-treated soil (0-10 cm) on north section

Selected soil samples were also sent undried to Enviro-Test Labs., Edmonton (ETL) for target polyaromatic hydrocarbon (PAH) analysis. A full description of their solvent extraction and GC/MS procedures is given in the Appendix. Four soil samples from 1986 were also sent to E. Peake at the Kananaskis Centre (University of Calgary) for similar target compound analysis as a quality-control check (see Appendix). Five groups of target PAH were chosen on the basis of preliminary work by ETL : naphthalenes, phenanthrenes, biphenyls, fluorenes and dibenzothiophenes.

In 1988 the solvent extract from selected soil samples, rather than the soil itself, was sent to ETL for PAH analysis, after evaporation to constant weight to remove the solvent. Harvested material was air-dried and weighed. Sub-samples were ground and analysed for %N. Dried and ground plant material was also sent to ETL for target PAH analysis. ETL's report is in the Appendix.

3. RESULTS AND DISCUSSION

A Progress Report (Ashworth, 1987) has been submitted which describes research findings in the first year of the field work. Some essential analytical data from that report are included in this report. There have also been several presentations of this work at waste disposal Conferences (Ashworth et al., 1988a & 1988b and Ashworth et al., 1989); some data from these reports are also included here.

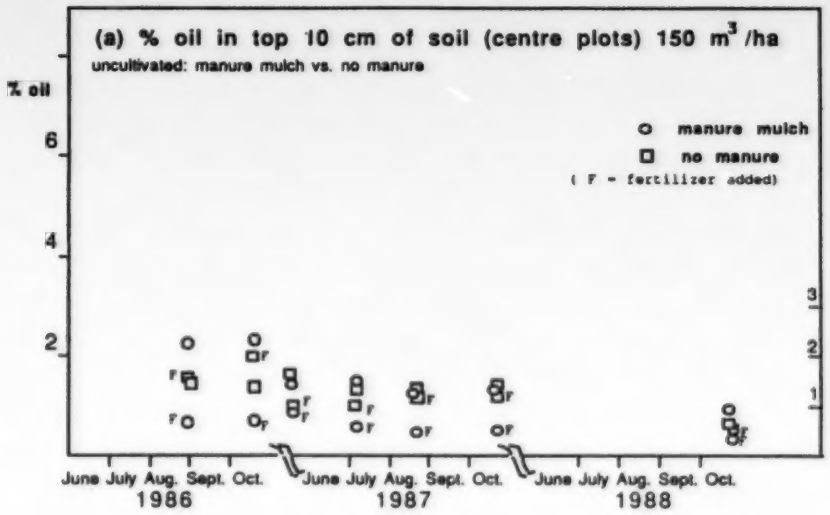
All results for 1986 were given in an Appendix to the Progress Report for that year (Ashworth, 1987). All results for 1987 and 1988 are summarized in Figures in the body of this Report and in Tables collected at the end. Some target hydrocarbon results are given in the Appendix.

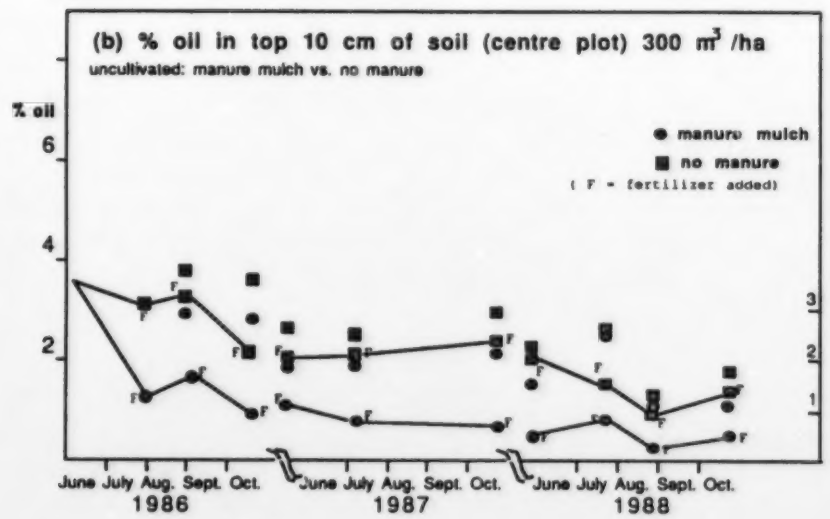
3.1 Salinity residue and soil pH

EC values fell rapidly in 1986 (Figure 2) especially where fertilizer had been applied, partly because of heavy summer rainfall (about 20 cm in July and another 16 cm in September). There was no growth because of this initial salinity, except for a few small seedlings that managed to grow at the low rate of application where manure had been left as a mulch. However, by fall 1987 EC values in soil from all treated plots had fallen below levels that restrict growth (see Table 1) and the hydrocarbon residue then became the limiting factor. For this reason EC values were not measured after October 1987. No damage to vegetation adjacent to the site was observed, indicating that salts leached down the profile and did not migrate over the soil surface. Summer 1987 was again wet, but relatively little rain fell in summer 1988.

3.1.1 Sub-surface salinity

Sub-surface salinity was at or below 4 dS/m on all plots by October 1987 (Table 2).


(a) % oil in top 10 cm of soil (centre plots) 150 m³ /ha
uncultivated: manure mulch vs. no manure
% oil
manure mulch
no manure
(F = fertilizer added)
June July Aug. Sept. Oct.
1986
June July Aug. Sept. Oct.
1987
June July Aug. Sept. Oct.
1988


(b) % oil in top 10 cm of soil (centre plot) 300 m³ /ha
uncultivated: manure mulch vs. no manure
% oil
manure mulch
no manure
(F = fertilizer added)
June July Aug. Sept. Oct.
1986
June July Aug. Sept. Oct.
1987
June July Aug. Sept. Oct.
1988

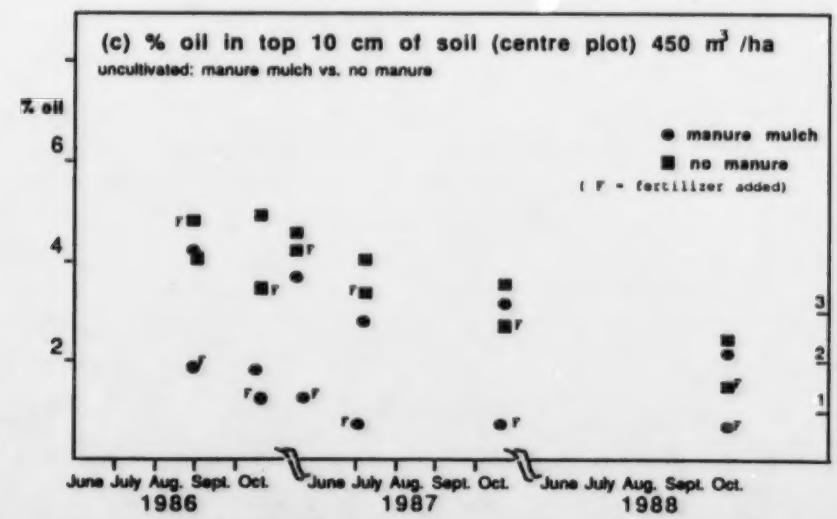

(c) % oil in top 10 cm of soil (centre plot) 450 m³ /ha
uncultivated: manure mulch vs. no manure
% oil
manure mulch
no manure
(F = fertilizer added)
June July Aug. Sept. Oct.
1986
June July Aug. Sept. Oct.
1987
June July Aug. Sept. Oct.
1988

Fig. 4. Oil content of DIMR-treated soil (0-10 cm) on centre section

3.1.2 Soil pH

Surface soil pH rose briefly after DIMR application. The highest pH observed was 9.3 at the top rate of DIMR application. This effect did not persist more than a few weeks; on June 23 the highest pH measured was 8.0 and thereafter all pH readings were near that of untreated soil (around 7.4).

3.2 Hydrocarbon degradation

3.2.1 Total hydrocarbons

Results of analysing surface soil (0-10 cm) for % oil have been condensed into Figs. 3, 4 & 5 which show how the total solvent-extractable hydrocarbons declined on the north, central and south group of plots respectively. Each Figure is in three parts (a, b & c, showing % oil at the low, middle and high rates of application respectively). One set of results (July 1987) is incomplete because sampling was terminated by heavy rain.

3.2.2 Effect of fertilizer on oil degradation

Symbols accompanied by the letter F indicate results for the fertilized portion of the individual plot given the treatment specified in the legend to the Figures. It can be seen that in virtually every pair of results the fertilized part of the plot has less oil.

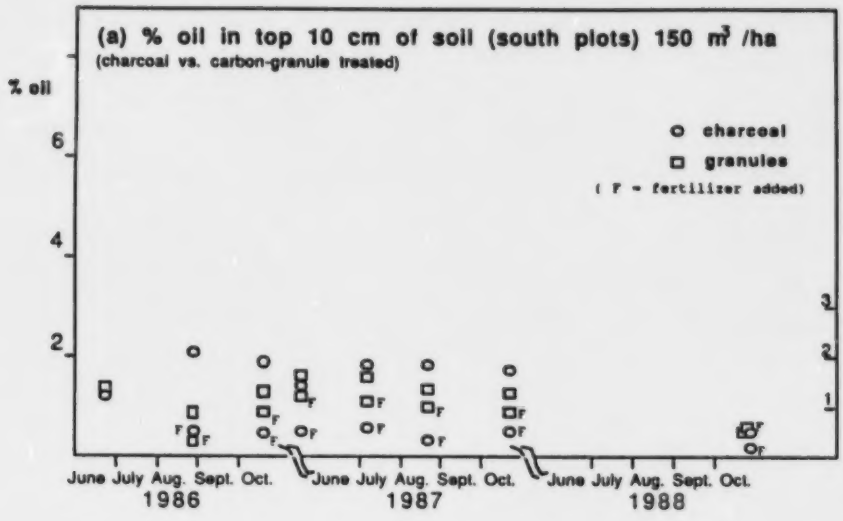
This holds true even for samples taken in the very early stages of the experiment; this gave rise to the suspicion that the DIMR was applied unevenly to the plots and was concentrated near the central, unfertilized strip. However, R. Glasrud was able to recall that care was taken during application to avoid a tendency for the DIMR to be dragged by the rototiller to the **ends** of the plots (Ashworth, 1987).

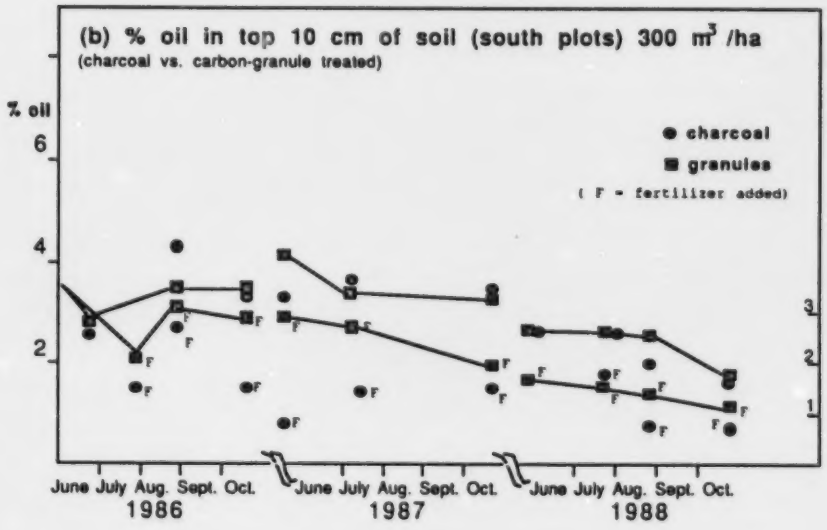
The first samples from treated plots were taken (on June 23, 1986) from both fertilized and unfertilized areas of each half-plot, on the unfortunate assumption that three weeks was too short a time for the fertilizer to have taken effect. Also, some analytical results obtained for this first set were spuriously low; the results in the Figures were obtained by reanalysis after long storage and are likely to be somewhat lower than the true value. Despite these uncertainties, the early beneficial effect of fertilizer applications on oil degradation seems to be genuine and parallels the lower salinity observed on the fertilized treatments (Fig.2)

3.2.3 Effect of manure on oil degradation

Manure cultivated into the soil appears by itself to have had little effect on oil degradation. This can be seen (Fig. 3) from the fairly close proximity of symbols representing unfertilized, unmanured soil (squares) and those representing manured soil (circles). These treatments are linked by lines in Fig. 3(b).

The manure mulch appears to have been about as effective in helping degrade oil as fertilizer applications alone. This observation is illustrated (see Fig. 4) by the fairly close coincidence of symbols corresponding to a manure mulch alone (circles), and fertilizer alone (squares with letter F).





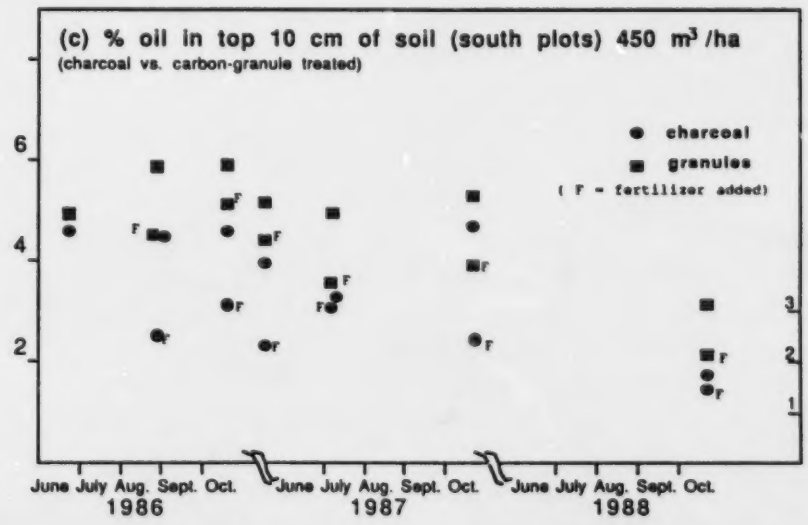


Fig. 5. Oil content of DIMR-treated soil (0-10 cm) on south section

The combination of manure and fertilizer was apparently the most effective in degrading oil, especially where the manure was left as a mulch. This effect can be seen (Fig. 4) from the wide separation of symbols representing manured and fertilized soil (circles with letter F) and soil with fertilizer alone (squares with letter F). These points are joined by lines at the 300 m^3 DIMR/ha rate (Fig. 4b).

Despite the care taken in DIMR application (section 3.2.2) it would seem from results in Figure 3 that the unmanured, fertilized end of the cultivated plot given 300 m^3 DIMR/ha got less than the intended rate. The manured, fertilized end got the intended rate; even so, % oil at this end rapidly fell to values similar to those at the other end (see grey squares and circles, each with letter F, in Fig. 3).

3.2.4 Effect of carbon amendments on oil degradation

In marked contrast to findings by Peake et al. (1986), in the lab and greenhouse phase of this study, both activated charcoal and spent carbon granules were ineffective and possibly even detrimental towards oil degradation (Fig. 5). This is tentatively ascribed to sorption of oil on the charcoal or carbon granules, with resulting lower availability of the hydrocarbons to degrading soil organisms (see section 3.4). Analysis of dilute solutions of PAHs in water is often accomplished after concentrating them by adsorption on carbon or polymer surfaces (Futoma et al., 1981).

The possibility that degradation was hindered because of high soil temperatures on the carbon-treated plots (because of absorption of solar radiation by the black soil on these plots) was discounted after cursory soil temperature measurements in summer 1988 using an integrating chemical method (Ashworth & Crépin, 1990) gave similar results for these plots and for plots without carbon.

3.2.5 Oil in the sub-soil

Subsurface samples (10-20 cm) consistently showed much smaller concentrations of hydrocarbons than surface soil (see Table 3). The highest concentrations found in this sub-surface layer were about 1.5 % oil at the 450 m^3/ha rate of DIMR, in 1986. However, sampling to this depth would include hydrocarbons originally incorporated below 10cm.

To get a reliable estimate of leaching into subsoil, small trenches were dug in October 1988 on plots given the 450 m^3/ha rate of DIMR, and replicate subsoil samples taken by augering at an angle through the bottom edge of the trench. These subsamples were virtually uncontaminated with material from nearer the surface. The mean weights of solvent-extracted material obtained after drying Soxhlet extracts to constant weight were 0.09, 0.10 and 0.07 % of soil from the fertilized plot given carbon granules, the unfertilized and uncultivated plot, and the fertilized/manure-mulched plots, respectively (30 cm depth). It was noticeable when trenching that surface soil from the manure mulched plot was light brown whereas in the trenches on the other two plots it was dark and oily. These results indicate very little leaching, since control samples

Fig. 6. Concentration (mg/kg soil) of phenanthrenes and C1-dibenzothiophenes during 1986 and 1987 growing seasons

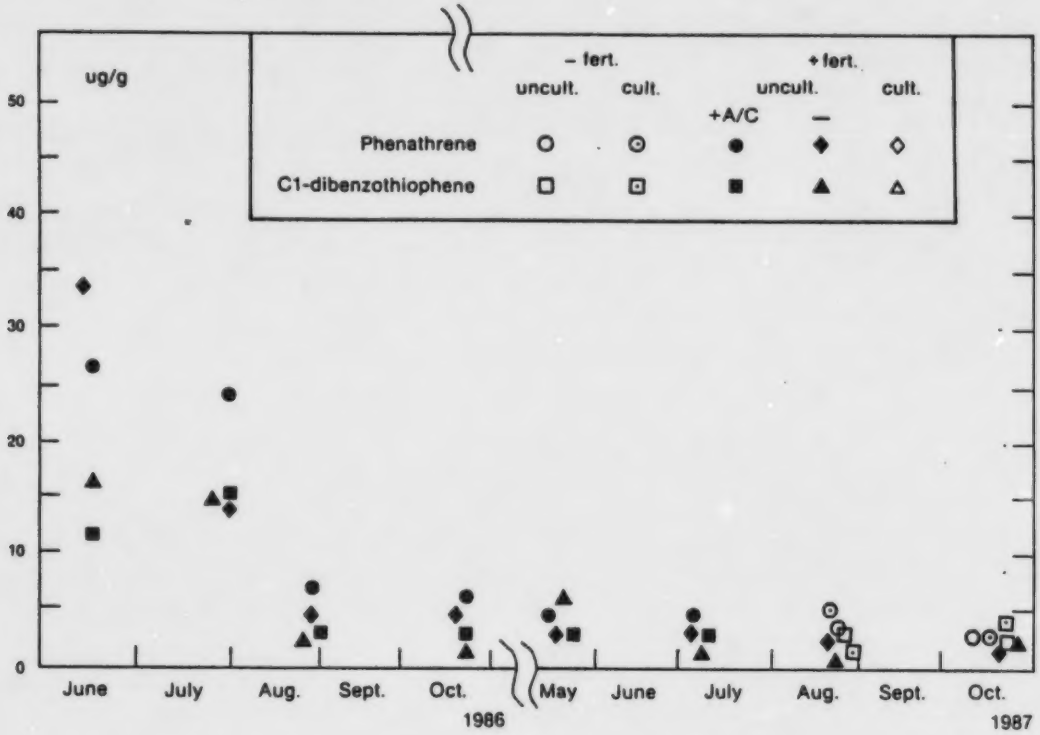


Fig. 7. Concentration (mg/kg soil) of biphenyls, fluorenes and C1-fluorenes during 1986 and 1987 growing seasons

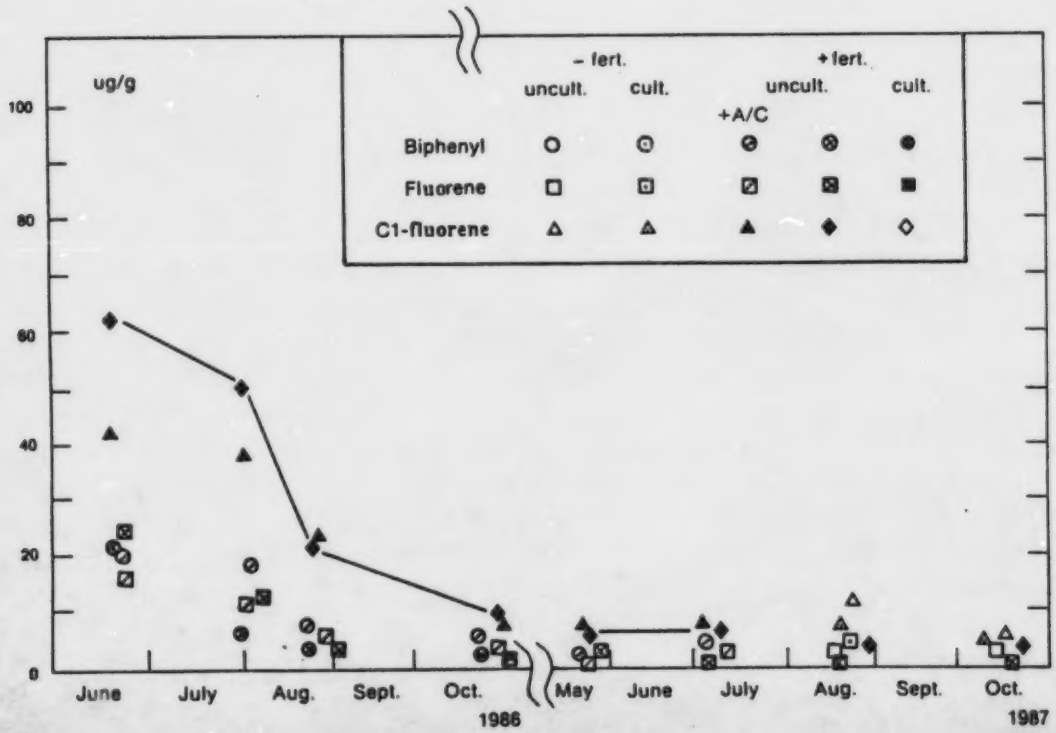


Fig. 8. Concentration (mg/kg soil) of substituted naphthalenes during 1986 and 1987 growing seasons

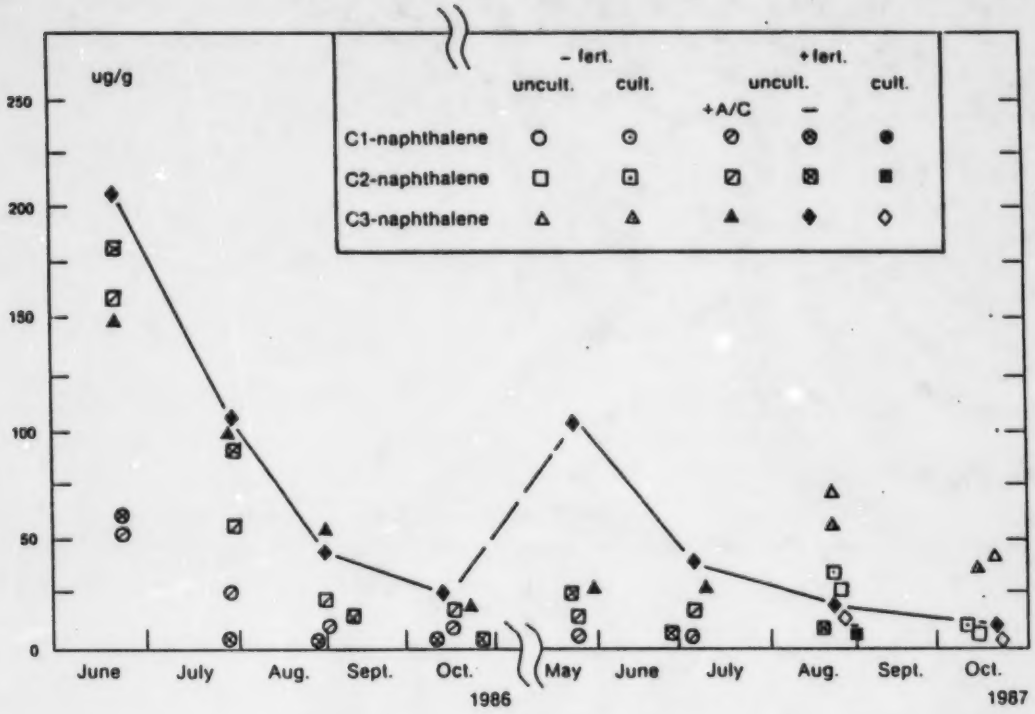
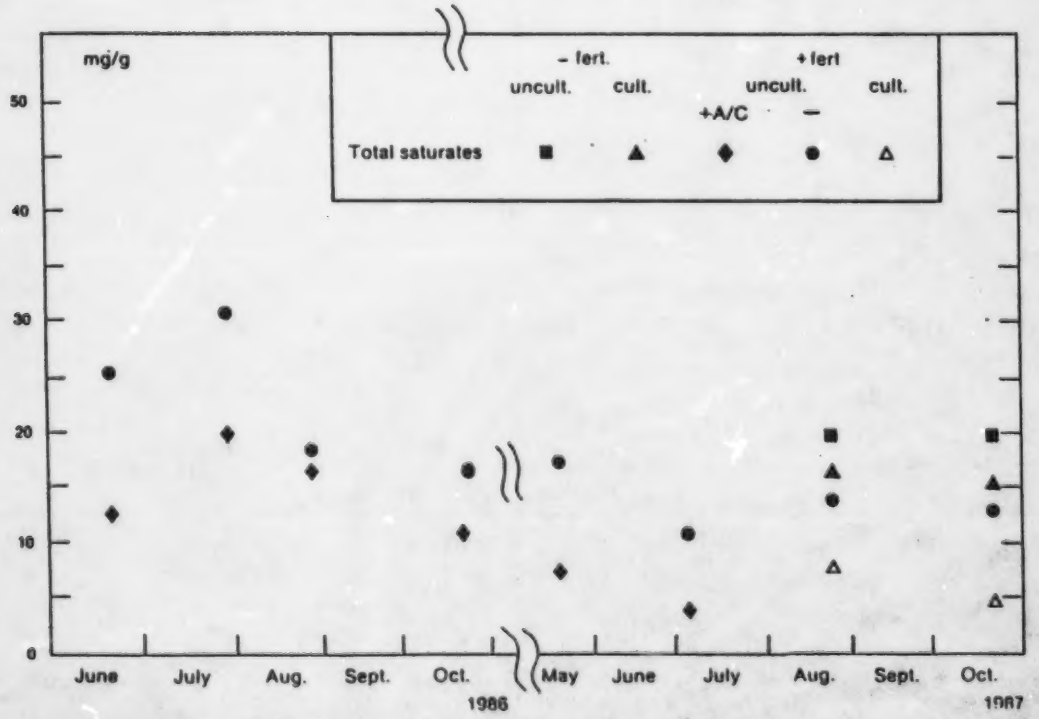


Fig. 9. Concentration (mg/ g soil) of saturated hydrocarbons during 1986 and 1987 growing seasons



typically give about 0.05% residue.

Watts et al. (1982) reported "negligible vertical migration of oil" after mixing waste engine oil at 210 m^3/ha into the top 15 cm of a sandy soil in an area receiving 120 cm of rainfall annually (roughly double the precipitation in the eastern Rocky Mountain foothills).

3.3 Target Hydrocarbons

Concentrations of target PAHs in soil given 300 m^3 of DIMR /ha declined rapidly in 1986 and generally continued to decline in 1987 (Figures 6-8). A marked discontinuity can be seen in results for substituted naphthalenes (Fig. 8). Despite checks by ETL this discrepancy was not resolved.

3.3.1 Aliphatics and aromatics.

GC measurements of saturated hydrocarbons, aromatic hydrocarbons and long-chain aliphatic hydocarbons (Figs. 9-11) were done on soil samples taken in 1986 and 1987. It can be seen that, in agreement with gravimetric % oil analysis results, large residues of these compounds persisted through 1987, even though the specific target PAHs had mostly declined to very small concentrations.

3.3.2 Quality Control in GC/MS work

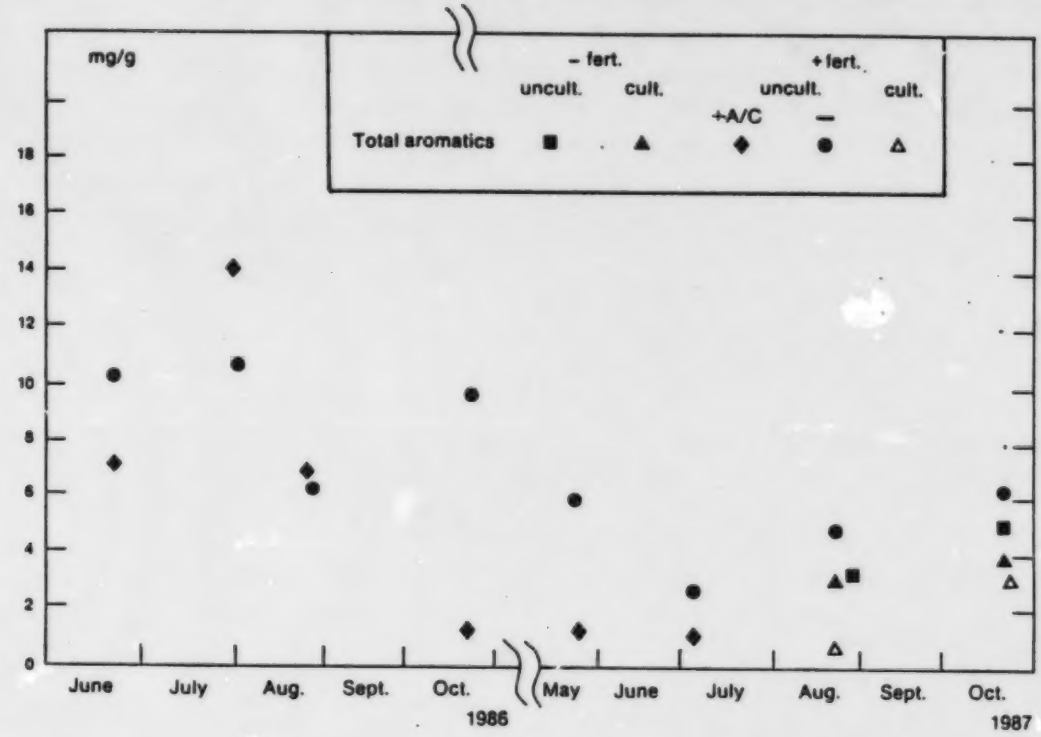
The results obtained by Peake (see Appendix) were in general in fair agreement with those of ETL for the various target PAHs for samples taken in 1986. Unfortunately 1987 samples were not checked for substituted naphthalenes in this quality-control work.

3.4 PAH degradation

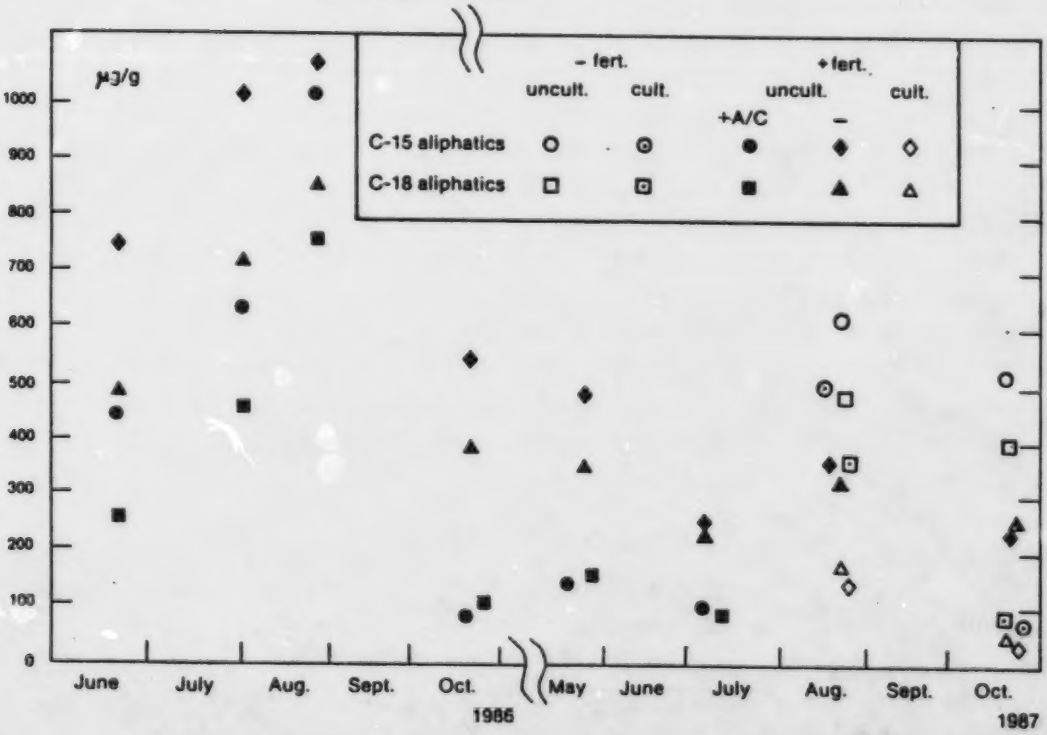
In the lab phase of this project, there was some resistance to degradation by PAH compounds (Peake et al., 1986). However, in the field study, degradation of all target PAHs was rapid even in the absence of applied fertilizer. All target compounds studied had half-lives of a few months only. These results are consistent with those obtained in a land treatment study by Lynch and Genes (1989).

Degradation by anaerobic organisms (Bakker, 1977; Sleat & Robinson, 1984; Tschech & Fuchs, 1987) may be important in the field, but may have been suppressed by the stringently aerobic conditions used in the lab work. (A cursory attempt to assess subsoil aerobicity by sampling the soil atmosphere at the site is described in a letter to D. McCoy shown in the Appendix. Air diffusion through the plastic of the bags used may have vitiated this experiment.) Alternative explanations for the slow degradation in the lab are that soil micro-organisms may have been subjected to intermittent moisture stress in the aerated soil columns used in the lab, or that a substrate necessary for degradation became limiting in the finite volume of soil used in the columns.

10. Concentration (mg/ g soil) of aromatic hydrocarbons during 1986 and 1987 growing seasons



11. Concentration (mg/kg soil) of long-chain aliphatic hydrocarbons during 1986 and 1987 growing seasons



3.4.1 Availability and Degradability of Hydrocarbons

Because of the commercial importance of agricultural herbicides and pesticides, the literature concerning the fate of these materials in soil is far more extensive than that concerning hydrocarbons. Since the principles involved in degradation are common to most classes of organic chemicals, concepts that have proved successful in predicting degradation rates of herbicides are directly relevant to the present purpose.

The "availability x degradability" concept of Briggs (1976) states that, because degradation takes place in the soil solution, relatively water-soluble, hydrophilic ("water-loving") chemicals will degrade faster than more lipophilic ("fat-loving") ones, because the latter are sorbed more strongly on soil organic matter. In particular, those hydrophilic compounds which lack substituent groups (chloro substituents, for example) that confer resistance to attack by microorganisms will degrade rapidly. Important factors controlling rates of degradation in soil are therefore (i) soil organic matter content, (ii) the hydrophilicity of the chemical and (iii) the nature of substituent groups attached to the molecule.

Relative hydrophilicity is frequently assessed by determining partition between water and a lipophilic solvent such as octanol. PAHs with low-to-medium molecular weights have small octanol/water partition coefficients (P), are therefore not very lipophilic and so are **available** to the soil solution. Also they have no substituent groups to confer resistance to attack on the molecule; hence, they are also **degradable**.

Rapid degradation of low-to-medium molecular weight PAH compounds (log $P < 6$), therefore, is to be expected on the basis of the Briggs (1976) approach.

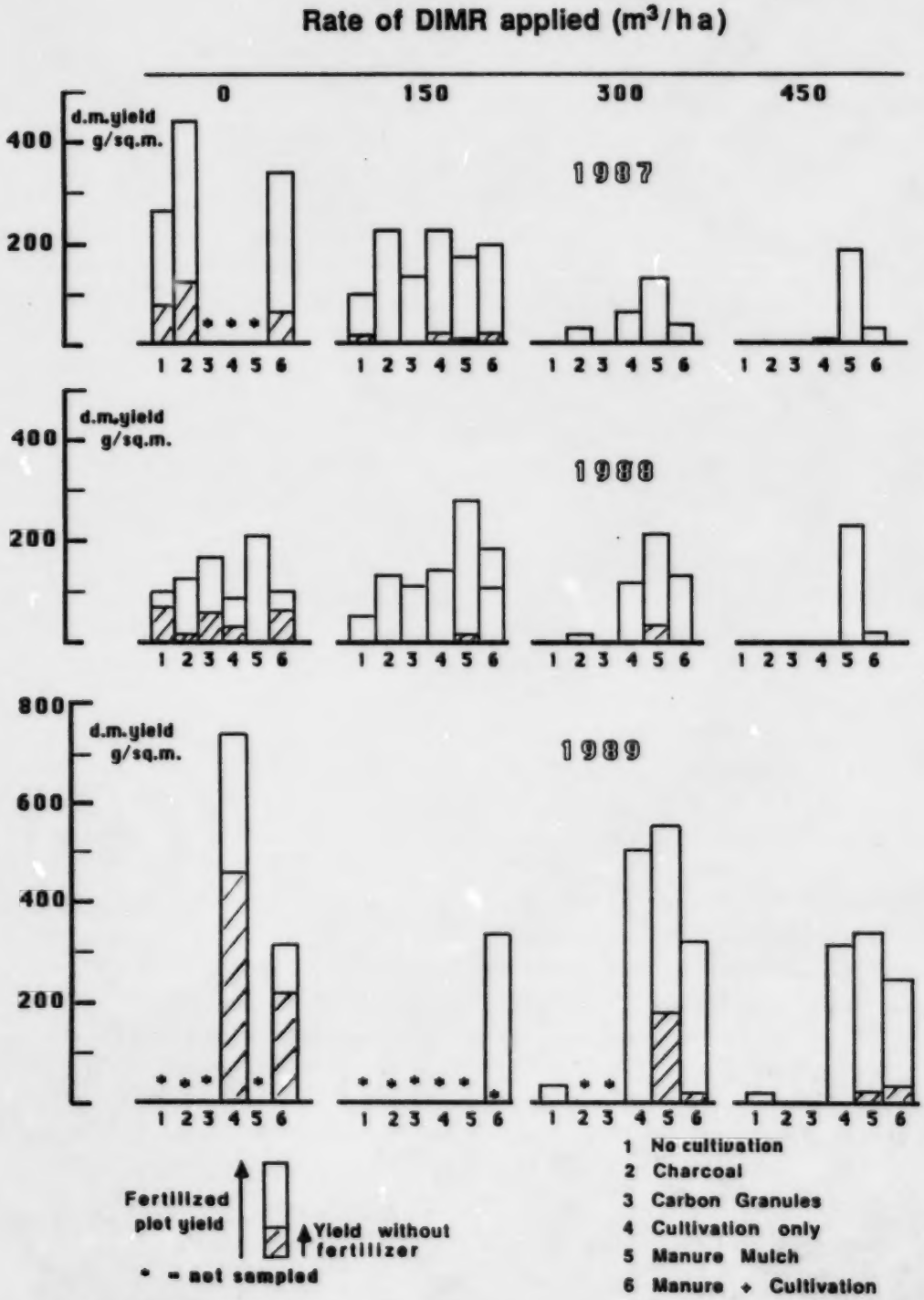
Later work by Briggs (1981) indicates that high molecular weight PAHs (four or more rings) which have high log P values (and therefore lower availability) would under Albertan conditions have half-lives of several years. Ultimately one might expect some incorporation of such long-lived materials into the stable "humus" fraction of soil organic matter. This is the goal of another oily waste land treatment field study currently being conducted by Dr. V. O. Biederbeck of Agriculture Canada near Maidstone, Saskatchewan. The objective of Biederbeck's work is to improve sandy soils low in organic matter, which have low moisture-holding capacity and are prone to erosion.

Work at Environment Canada's Wastewater Technology Centre (T. L. Bulman, personal communication) has shown that low M.W. PAHs are also incorporated into soil organic matter. Bulman suggests that low M.W. compounds will be incorporated into humus more rapidly than high M.W. ones and that, once incorporated, they will be as resistant to degradation as high M.W. compounds.

3.4.2 Mobility of organics in soil

Despite the "availability" of PAHs referred to above, their water solubility is very limited in absolute terms and they would not be expected

Fig. 12. Dry matter yields (g/m^2) in 1987, 1988 & 1989



to be mobile in soil with several percent organic matter. This was confirmed at the site by the absence of target PAHs in solvent extracts from sub-soil samples. These samples also gave near-background results for their total % oil content (section 3.2.5).

In laboratory studies using repeatedly leached columns of sandy loam soil, no PAHs were found more than 15 cm below the zone of their incorporation in the column (Symons et al., 1988).

3.5 Vegetative Growth

As already mentioned, soil salinity was so high in 1986 that no growth was possible until after July 1987 (see Plates 1-6). However, salinity was not then a limiting factor. The growth of vegetation in 1987 and 1988 corresponded with the extent of degradation of the oil residue. In terms of both plant growth and oil degradation the treatments ranked in the following order : unfertilized plots (worst) < fertilizer & spent granules < fertilizer & charcoal < fertilizer and cultivation < fertilizer & manure cultivated in < fertilizer and manure left as a mulch (best).

After July 1987, and in 1988 all plots treated with the low rate of DIMR and fertilizer had good growth and more than 80% surface coverage (Plates 8, 10 and 12). However, at the higher rates of DIMR application (Plates 7, 9 and 11), only the fertilized ends of plots given a surface mulch of manure had reasonably good coverage (75%) and growth (Plate 9).

In 1989, all fertilized plots had good coverage and grass growth except those given the highest rate of DIMR application. The fertilized and cultivated plot given this rate (Plate 23) had more growth than the corresponding uncultivated plot (Plate 22). There was still little or no growth on the unfertilized middle section of each plot but some coverage where manure had been applied (Plate 24).

3.5.1 Yield and %N of dry matter

Yields are approximate because growth was not uniform, especially on plots given high DIMR rates. Yields (Table 4 & Fig. 12) were generally consistent with % oil on the plots. Plants on fertilized plots had consistently higher protein content (see %N results, Table 5).

Vegetation tended to become established when the residue of oil fell below 1% of the total weight of soil. This had still not occurred by the end of 1988 where no fertilizer had been applied and, on plots given fertilizer plus charcoal, only fell to that level in 1988. This 1% threshold is not absolute but depends largely on the quantity of low molecular weight hydrocarbons added to the soil (Rowell, private communication). Soils given higher rates of oil or heavier grades of oil are likely to have higher revegetation thresholds. Danielson et al. (1988) reported a 3% threshold for soils treated with oily sludges.

A noticeable feature of the manure-mulched plots was that the surface cover trapped dead leaves and other organic debris, thereby adding to the existing thin veneer of material. This discontinuous layer has two desirable properties; it is uncontaminated at first, and it acts as a mulch conserving soil moisture. In July 1987, on disturbing loose portions of this surface layer, healthy seedlings could be seen in damp patches underneath.

3.6 PAHs in vegetation

Dried and ground plant material taken in fall 1987 from a control plot and from a fertilized plot given the manure mulch (300 m^3/ha DIMR rate) had no detectable target PAHs but traces (0.2 - 0.5 ppm of each target compound) were found in the small amount of plant material harvested from the fertilized plot with activated charcoal.

When the above tests were repeated on plant material taken in fall 1988, traces of target PAHs were found in all the samples (see Report from Enviro-Test Labs in the Appendix). Concentrations of this magnitude can be accounted for by contamination due to soil on leaves and stems, but sorption of vapour by leaves is another possible mechanism of contamination.

Plant uptake of compounds such as PAHs with octanol:water partition coefficients (P) of greater than 1,000 is unexpected; chemicals generally have to be more hydrophilic than this (i.e. log P < 3) in order to be active systemically (Briggs, pers. comm.). Bell et al. (1988) commented that "Pollutants with the highest log P values, for example . . the PAHs (4.1 - 7.7) are those most likely to be accumulated by or in the root and not be translocated out of it." No PAH uptake has been observed in recent growth chamber ("microcosm") experiments using split-root techniques and ^{14}C-labelled PAHs (Webber, 1989; Biederbeck and St. Jacques (1988) found no PAH contamination of grain or straw when wheat was grown on soil treated with oily sludge. However, Beall and Nash (1971) reported that root uptake of organochlorines with high log P values was as important as vapour sorption by soybeans.

3.7 Most successful species

Seed heads in the dried produce from each plot were examined in the laboratory. In 1987, perennial ryegrass was most frequently the dominant species present (about 3:1 over the next most prominent grass, timothy).

In 1987, oats worked well as a nurse crop. Their value consists largely in providing ground cover in the current season and a residue of biomass to support subsequent growth of permanent forage.

In 1988 the oats were absent and crested wheatgrass joined the other two dominant species. Alkaligrass and (rarely) slender wheatgrass were the only other species identified; winter wheat did very badly.

4. CONCLUSIONS

Revegetation of soil treated with DIMR at 150, 300 or 450 m^3/ha was achieved with minimal environmental impact after three seasons on plots given fertilizer and a manure mulch. Fertilization and cultivation gave good results after three seasons at the lowest rate of application, but required an extra season at the higher rates. In the season of application of DIMR, salinity was the major factor preventing seedling establishment; in later years the hydrocarbon residue was the sole limiting factor. Revegetation was not successful if fertilizer was withheld. Activated charcoal or carbon granules were detrimental to degradation, possibly because they sorbed hydrocarbons and rendered them less available to attack by degrading organisms.

There was very little downward movement of oil in the treated soil and little or no uptake of target polyaromatic hydrocarbons by plants growing on the treated soil.

This field trial has provided very useful information for those trying to gauge the acceptability of land treatment as a disposal option for DIMR. However, two questions are outstanding: (1) How typical is this one site? (2) Will practitioners in the energy industry be prepared to sustain the intensive management effort needed for safe reclamation at their sites?

It is in the interests of the energy industry for them to fund further trials of this nature at other locations. The soil at our site was fairly slow to drain and not rich in organic matter. Low permeability is of course a disadvantage because salts in the added DIMR disperse slowly. Lower organic matter content is a disadvantage because the risk of leaching of hydrocarbons is greater. Our site was also at high elevation, with a relatively short growing season and in consequence relatively slow degradation. Other soils at less exposed sites may prove to be better suited to DIMR land treatment.

Also, this trial suffered from having to serve as a demonstration site as well as a test-bed for ideas on land treatment of DIMR, and its subsequent degradation. Lack of replication of treatments means that many observations have to be regarded as tentative.

ACKNOWLEDGEMENTS

R.P. Scroggins (Environment Canada) and D. McCoy (Husky Oil; ERAC representative) contributed much information and valuable help throughout the project in addition to being responsible for administration and funding. R.D. Glasrud managed the field site. D. Erickson and colleagues at Enviro-Test Labs did the target organics analyses. R. Kirk and R. Jones of Norwest Labs did most of the other analyses. C. Engler identified seeds from the site. A draft report was constructively reviewed by H.R. Sims and C. Powter of Alberta Environment, R.E. Byers and L.T.L. Callow of Gulf Canada Resources Ltd. and T. Bulman of Environment Canada. C. Meloche supplied references to anaerobic degradation.

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Table 1. Electrical Conductivity (dS/m) of topsoil (0-10cm) October 1986 & 1987

Treatment		Rate of DIMR applied (m^3/ha)							
		0		150		300		450	
		+F	-F	+F	-F	+F	-F	+F	-F
				12[i]		23[i]		34[i]	
None	Oct. '86	-	-	2.9	4.3	3.9	6.2	3.7	9.1
	Oct. '87	-	-	1.6	1.7	2.0	2.5	2.3	2.4
Charcoal	Oct. '86	-	-	4.6	6.5	5.5	8.4	10.3	10.3
	Oct. '87	-	-	0.9	1.9	2.2	2.4	3.5	2.9
C granules	Oct. '86	-	-	2.5	4.1	4.5	7.0	5.1	12.0
	Oct. '87	-	-	1.3	2.0	2.2	2.7	2.1	2.8
Cultivation only	Oct. '86	-	-	2.5	4.4	4.5	6.0	6.8	11.9
	Oct. '87	-	-	1.8	1.6	1.5	1.9	2.0	1.6
Manure mulch	Oct. '86	-	-	2.9	4.0	3.7	3.3	4.4	7.5
	Oct. '87	-	-	1.2	1.5	1.6	1.8	1.6	2.2
Manure + Cultivation	Oct. '86	-	-	3.0	3.5	6.1	6.8	7.1	6.9
	Oct. '87	-	-	1.2	1.7	1.7	1.7	2.4	1.7

\- background value (0.5 dS/m approx.)
i = approx. initial value, June 1986

Table 2. Electrical Conductivity (dS/m) of subsoil (10-20cm) October 1986 & 1987

Treatment		Rate of DIMR applied (m^3/ha)							
		0		150		300		450	
		+F	-F	+F	-F	+F	-F	+F	-F
				12^i		23^i		34^i	
None	Oct. '86	-	-	3.0	4.5	4.0	5.9	3.7	10.0
	Oct. '87	-	-	1.8	2.4	2.1	2.6	2.3	3.2
Charcoal	Oct. '86	-	-	2.0	1.8	4.6	5.6	7.7	9.3
	Oct. '87	-	-	n	1.5	2.2	2.5	4.1	2.8
C granules	Oct. '86	-	-	2.4	3.3	4.1	5.9	6.6	11.2
	Oct. '87	-	-	1.0	1.7	2.0	2.6	1.8	4.0
Cultivation only	Oct. '86	-	-	3.1	5.2	5.7	6.8	5.5	9.2
	Oct. '87	-	-	n	1.9	1.4	2.1	2.2	1.7
Manure mulch	Oct. '86	-	-	3.0	4.6	5.5	4.2	5.2	6.8
	Oct. '87	-	-	n	2.2	n	2.3	n	2.0
Manure + Cultivation	Oct. '86	-	-	3.4	4.0	6.3	7.2	5.3	6.2
	Oct. '87	-	-	n	1.7	n	2.1	n	1.9

- background value (0.5 dS/m approx.)
n = not sampled (sampling subsoil was difficult on areas of good growth)

Table 3. **Oil content (%) of sub-soil (10-20cm) October 1986, 1987 & 1988**

Treatment		Rate of DIMR applied (m^3/ha)							
		0		150		300		450	
		+F	-F	+F	-F	+F	-F	+F	-F
				1.8[i]		3.6[i]		5.3[i]	
None	Oct. '86	-	-	0.2	0.1	0.1	0.2	0.5	0.7
	Oct. '87	-	-	L	L	0.2	1.2	0.6	1.4
	Aug. '88	-	-	n	n	0.3	0.1	n	n
Charcoal	Oct. '86	-	-	L	0.1	0.2	0.3	0.3	0.2
	Oct. '87	-	-	n	0.1	L	0.5	0.8	1.1
	Aug. '88	-	-	n	n	0.2	L	n	n
C granules	Oct. '86	-	-	0.1	0.1	0.3	0.4	0.8	1.1
	Oct. '87	-	-	L	0.1	0.2	0.4	1.4	1.9
	Aug. '88	-	-	n	n	0.1	L	n	n
Cultivation only	Oct. '86	-	-	0.1	0.4	0.2	0.5	0.3	1.6
	Oct. '87	-	-	n	0.2	L	L	0.2	1.1
	Aug. '88	-	-	n	n	0.2	0.2	n	n
Manure mulch	Oct. '86	-	-	0.1	0.3	L	0.1	L	0.7
	Oct. '87	-	-	n	0.1	n	1.0	n	1.3
	Aug. '88	-	-	n	n	L	0.2	n	n
Manure + Cultivation	Oct. '86	-	-	0.5	0.2	0.3	n	0.2	0.8
	Oct. '87	-	-	n	0.2	n	0.1	n	1.2
	Aug. '88	-	-	n	n	0.2	0.3	n	n

L = less than 0.1%; n = not sampled; i = approx. initial value (June, 1986)

Table 4 . **Dry Matter Yields (g/m^2)**
October 1987, 1988 & 1989

Amendment		Rate of DIMR applied (m^3/ha)							
		0		150		300		450	
		+F	-F	+F	-F	+F	-F	+F	-F
None	Oct. '87	270	80	100	16	-	-	-	-
	Oct. '88	100	70	60	-	-	-	-	-
	Oct. '89	n	n	n	n	29	-	7	-
Charcoal	Oct. '87	450	120	220	-	37	-	-	-
	Oct. '88	120	17	140	-	13	-	-	-
	Oct. '89	n	n	n	n	n	-	-	-
C granules	Oct. '87	n	n	140	-	-	-	-	-
	Oct. '88	170	60	110	-	-	-	-	-
	Oct. '89	n	n	n	n	n	-	-	-
Cultivation only	Oct. '87	n	n	220	16	61	-	13	-
	Oct. '88	90	34	150	n	120	-	-	-
	Oct. '89	751	465	n	n	490	2	309	-
Manure mulch	Oct. '87	n	n	180	8	130	-	190	-
	Oct. '88	210	210	280	15	210	32	230	-
	Oct. '89	n	n	n	n	565	177	358	14
Manure + Cultivation	Oct. '87	340	70	200	17	41	-	37	-
	Oct. '88	100	60	190	110	140	-	27	-
	Oct. '89	300	211	342	n	317	12	239	23

- less than 2 g/m^2 n = not sampled

Table 5 .

%N in Dry Matter
October 1987 & 1988
(not measured 1989)

Treatment		Rate of DIMR applied (m^3/ha)							
		0		150		300		450	
		+F	-F	+F	-F	+F	-F	+F	-F
None	Oct. '87	2.0	0.9	1.6	1.8	-	-	-	-
	Oct. '88	1.1	0.9	1.0	-	-	-	-	-
Charcoal	Oct. '87	2.2	1.0	1.7	-	2.0	-	-	-
	Oct. '88	1.0	0.8	0.9	-	1.2	-	-	-
C granules	Oct. '87	n	n	1.9	-	-	-	-	-
	Oct. '88	1.3	0.9	0.9	-	-	-	-	-
Cultivation only	Oct. '87	n	n	2.3	-	1.7	-	1.9	-
	Oct. '88	1.0	-	0.8	-	-	-	-	-
Manure mulch	Oct. '87	n	n	2.1	0.9	1.6	-	1.5	-
	Oct. '88	0.9	0.7	1.5	0.5	1.1	0.7	1.0	-
Manure + Cultivation	Oct. '87	1.2	1.0	2.2	0.8	1.7	-	2.2	-
	Oct. '88	1.7	1.3	0.8	0.6	0.9	-	0.9	-

n = not sampled - means no growth

APPENDIX

Metals in DIMR (Norwest Labs analysis) 1986

EnviroTest Labs analytical procedures for organics in DIMR and target compound identification, July 1986

Quality Control work done by Kananaskis Centre on target hydrocarbons, dated June 4, 1987

Memo to David McCoy, re: soil atmosphere sampling dated June 1, 1988

Report from Enviro-Test Labs on analysis for target hydrocarbons in plant and soil samples, dated March 1989

Norwest Soil Research

Results of analyzing for metals in invert cuttings twice by digestion/ICP and once in ICP analysis of leachate.

Element	W/O 12559	W/O 12696	Leachate W/O 12560
Ti	2,900	2,800 ug/g	L0.001 mg/l
V	83	110	0.011
Cr	59	23	L0.002
Mn	180	190	L0.001
Fe	21,000	21,000	L0.003
Co	6.5	7.5	L0.005
Ni	27	25	L0.01
Cu	27	37	L0.005
Zn	180	250	L0.005
As	N.D.	8.5	0.0013
Hg	0.19	0.13	L0.0002
Se	0.04	L0.02	0.0008
Be	0.94	1.1	L0.001
Ca	34,000	35,000	200
Mg	13,000	12,000	0.19
K	11,000	14,000	11
Sr	630	490	3.2
Mo	L3.0	3.0	L0.01
P	500	300	L0.1
Pb	17	8.0	L0.05
Ba	430	150	0.36
Al			
B			
Na			
Zr			
Bi	L10	L10	L0.2
Cd	L0.10	L0.25	L0.002
Li	L50	L50	L0.05
Th	L2.5	L2.5	L0.05
U	L10	L15	L0.2

L = less than

N.D. = not done

ETL Enviro-Test Laboratories
A Division of ETL Chemspec Analytical Limited
9936 - 67th Avenue — Edmonton, Alberta T6E 0P5 Telephone: (403) 434-9509

CHEMICAL ANALYSIS REPORT

NORWEST LABS Date: July 11, 1986

Lab Sample #: 06-86-783 Sampled By: _____

Customer #: _____ Date Received: June 6/86

Sample Description: 6 replicate diesel invert drilling mud residues (DIMR's). Two replicates for full GC/MS characterization and gravimetric quantitation. 6 replicates for extraction and GC/FID fingerprinting.

OVERVIEW:

Six DIMR's were received from Norwest Labs. The samples were spiked with deuterated surrogates and soxhlet extracted with dichloromethane (DCM). The DCM extracts were extracted with aqueous sulphuric acid to isolate the basic organics from the neutrals. The basic fraction was injected on GC/MS to determine if any hetero-cyclic nitrogen compounds (HNC's) were present. The neutral fractions were fractionated on alumina to isolate three fractions; an aliphatic fraction, an aromatic fraction and a polar fraction. The aromatic fraction were characterized using gas chromatography/mass spectrometry (GC/MS). The three fractions were also determined gravimetrically using the same method as the Kananaskis Centre ("Biodegradation and Analysis of Diesel Invert Mud Residues, Phase I)

Also all six samples were soxhlet extracted with DCM and analyzed by gas chromatography/flame ionization detection (GC/FID). This test was completed to establish a standard fingerprint for the DIMR's and to determine if all six samples were similar in composition and concentration.

LIST OF SAMPLES SUBMITTED:

LAB SAMPLE #	SAMPLE I.D.	TESTS PERFORMED
06-86-783-1	12546,1	GC/FID, GC/MS, Gravimetric
06-86-783-2	12546,2	GC/FID, GC/MS, Gravimetric
06-86-783-3	12546,3	GC/FID
06-86-783-4	12546,4	GC/FID
06-86-783-5	12546,5	GC/FID
06-86-783-6	12546,6	GC/FID

METHODS:

All six samples were dried at room temperature overnight. The oily wet samples were then mixed with granular sodium sulphate and soxhlet extracted with DCM for 16 hours. Two of the samples were spiked with a series of deuterated PAH's and one deuterated HNC to determine the method efficiencies.

The DCM extract B/N fraction from the two spiked samples is further extracted with 6N H_2SO_4 to separate the basic compounds (HNC's) from the neutral compounds. The DCM fraction (Neutral) is taken to near dryness and dissolved in 2ml of hexane. The hexane is quantitatively added to an 18g alumina column. The separation efficiency of each freshly treated batch of alumina was checked by adding to the alumina a standard mixture of diesel and selected

polycyclic aromatic hydrocarbons (PAHs). If separation of aliphatics from the PAHs was achieved the alumina was considered adequate for the samples. The alumina column is eluted with 45ml of pentane to isolate the non-polar saturated hydrocarbons (Fr. 1) then by 150ml of benzene to isolated the aromatics (Fr. 2) followed by 150ml of DCM to isolated the polar compounds (Fr. 3). All three neutral fractions are reduced to a known volume and analyzed by GC/FID. The aromatic fraction (Fr. 2) is further characterized by GC/MS. The acidic aqueous portion (Base compounds) is adjusted to pH $\geq$10 with 6N NaOH and extracted with DCM to isolate the basic (HNC) compounds. The DCM is reduced to a known volume and analyzed by GC/MS.

In addition to the instrumental analysis gravimetric analysis was also performed on the two samples that were fractionated on alumina. Fractions from the alumina were dried using roto-vap and nitrogen blow-down and then weighed.

RESULTS:

The results are presented as follows:

1. Results of quality control surrogate spikes - Table 1
2. Overall composition of invert shale extractable organic material - Table 2
3. Results of total hydrocarbons extracted for all the samples as well as the two samples that were fractionated on alumina - Table 3
4. Results of target HNC GC/MS analysis.
5. Summary of Identification by GC/MS of the aromatic fractions of two selected samples.
6. Total ion GC/MS chromatograms for the aromatic fractions.

7. Total ion GC/MS chromatograms for the base (HNC's) fraction.
8. GC/FID chromatograms of all six samples before any clean-ups.

The recovery of naphthalene-d_8 and acenaphthene-d_{10} are down (Table 1) but are consistent with recoveries we have routinely been achieving in similar samples. These more volatile PAHs appear to be lost during the evaporation and the nitrogen blow-down steps. The recoveries of the remaining surrogates are good in both samples and the duplicate results show good agreement.

The DIMR's are basically composed of saturated hydrocarbons 92 to 93% (Table 2) with only 5 to 6% aromatics and 1% polar material.

The total hydrocarbons by GC/FID (Table 3) for all the samples agree well with the exception of sample 738-3. Also the totals by GC/FID agree well with the gravimetric percentage of total sample. All six samples have identical GC/FID fingerprints and thus are assumed to be similar in composition (See attached chromatograms).

Analyzing future samples for HNC's would not be advisable as no target HNC's were detected in the sample. The method for HNC's was proven efficient by the 71% and 76% recovery of Quinoline-d_7.

Judging from the specific compounds identified by GC/MS it is our suggestion that the following groups be used as target compounds for subsequent analysis.

1) Dimethyl naphthalenes
2) Phenanthrene
3) Biphenyls
4) Fluorene
5) Dibenzothiophene

Benzo(a)pyrene would be dropped from the list because it was not detected in the samples.

TABLE 1

RESULTS OF QUALITY CONTROL SURROGATE SPIKES

SURROGATE	SAMPLE 783-1 (Recovery)	SAMPLE 783-2 (Recovery)
Naphthalene-d_8	34%	40%
Biphenyl-d_{10}	62%	71%
Acenaphthene-d_{10}	45%	43
Dibenzothiophene-d_8	90%	95%
Chrysene-d_{12}	91%	100%
Quinoline-d_7	76%	71%

Samples were spiked at 40 to 50ppm.

TABLE 2

OVERALL COMPOSITION OF INVERT SHALE EXTRACTABLE ORGANIC MATERIAL, GRAVIMETRIC RESULTS

SARCEE	ALIPHATIC %	AROMATIC %	POLAR %	% OF TOTAL SAMPLE
Sample #783-1	92%	6%	1%	10.5%
Sample #783-2	93%	5%	1%	10.7%

THE UNIVERSITY OF CALGARY
2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

RECEIVED
JUN 08 1987
KANANASKIS CENTRE FOR ENVIRONMENTAL RESEARCH

Telephone Campus (403) 220-5271
Telephone Kananaskis (403) 220-5355

June 4, 1987

Dr. John Ashworth,
Northwest Soil Research Ltd.,
9938 - 67 Avenue,
Edmonton, Alberta T6E 0P5

Dear John,

The four samples of soil which were treated with diesel invert mud residue have been analyzed as per the method used by Enviro-Test. The samples were air dried as described in the method. This probably results in the loss of lighter hydrocarbons, possibly including some naphthalene, therefore, the measured concentration may differ from the actual concentration at the time the soil samples were taken in the field.

Many of the more readily identifiable hydrocarbons are lost from the DIMR-soil mixture in the field by evaporation, biodegradation, and possibly leaching down the soil profile. The remaining oily material is a very complex mixture containing numerous isomers of many substituted aromatic compounds which are often difficult to identify and measure quantitatively. This is illustrated by the chromatogram of sample 1015-2. In addition to the specified target compounds listed in tables 1, 2, 3, and 4, compounds such as C_1, C_2, C_3, and C_4 substituted biphenyls, phenanthrenes, pyrenes, and dibenzathiophenes were identified. The highest concentrations of the target aromatic compounds were found in samples 832-5 and 1015-2 taken from the top 10 cm of soil on June 23 and July 31, respectively. The relative amounts of the target aromatic compounds was somewhat different in the two samples with relatively more total C_3-naphthalenes in the 1015-2 sample. The amounts of individual C_3 naphthalene isomers were greater and more isomers were detected. This is somewhat puzzling and seems unlikely to be caused by degradation. Possibly the DIMR was not uniform in composition.

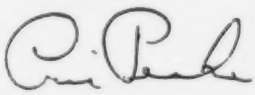
The sample taken October 23 from a depth of 0-10 cm, 11507, showed lower concentrations of aromatics, probably as a result of biodegradation. Sample 1015-11 was interesting since it was collected from a depth of 10-20 cm. Low concentrations of naphthalenes were found in the sample. These compounds may have migrated downward in the soil profile or perhaps the soil was tilled to a depth greater than 10 cm on occasion, or the 10-20 cm sample may have been contaminated with 0-10 cm soil during sampling.

.../2

The raw GC/MS data will be retained for future interpretation, if required. Northwest soils will be billed by the University for the analyses. The total cost will be $2,000.00.

Should you have any questions, please call me at 220-3194.

Sincerely,



EP/dlp
enclosures

Eric Peake
Professional Associate

Appendix Item 3. Quality Control Work; Target Organics Analysis.

Comparison of Results Obtained by EnviroTest Labs (Edmonton) and Kananaskis Centre (Calgary) for 4 soil samples taken in 1987.

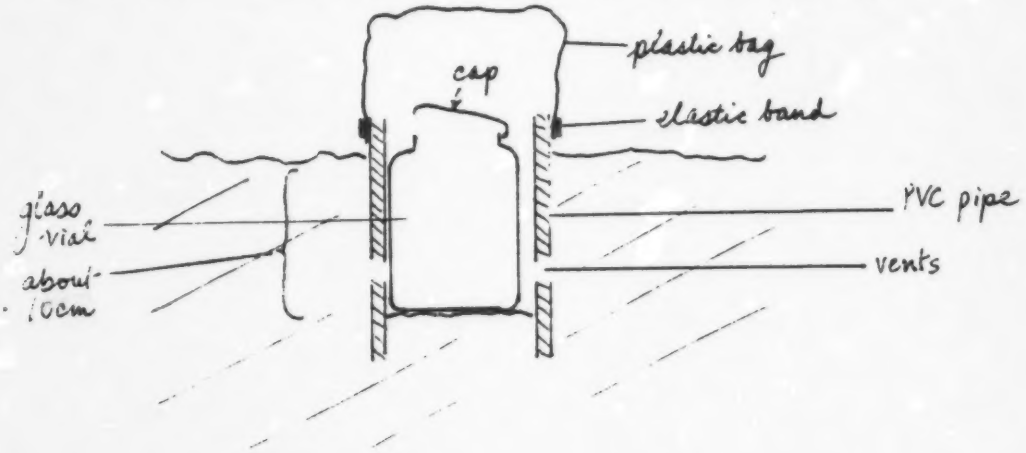
	Sample number, date & depth							
	832-5, June 23 0-10 cm		1015-2, July 31 0-10 cm		1015-11, July 31 10-20 cm		11507, Oct.23 0-10 cm	
	All results are in mg of compound per kg of dry soil							
Compound	Kan.	ETL	Kan.	ETL	Kan.	ETL	Kan.	ETL
Naphthalene	3	9	4	8	0.3	0.3	0.9	2
C2-Napthalenes	107	60	37	28	1.2	1.0	9.3	7
C2-Napthalenes	299	170	146	70	0.8	1.5	17	9
C2-Napthalenes	122	215	27	101	6.7	10	24	11
Biphenyls	12	26	9	19	0.3	2	3	6
Fluorenes	13	27	4.5	11	ND	1	0.7	3
C2-Fluorenes	90	78	72	44	ND	6	ND	5
Phenanthrene	32	24	18	26	0.1	2	1.9	5
C2-Dibenzothiophene	26	19	24	16	ND	2	10.7	2

Kan. = Result obtained by Kananaskis Centre
ETL = Result obtained by EnviroTest Labs
ND = None Detected
No quinoline, carbazole, dibenzo(a,h)acridine or benzo(a)pyrene-type compounds were detected by ETL or by Kananaskis.

Memo to David McCoy, Canterra Energy Ltd.

Subject: Soil atmosphere sampling, Sarcee Invert Cuttings site
June 1, 1988.

Soil air samples (100 mL) were taken using a PVC-pipe chamber, perforated near the base and sealed off from the open air with a plastic bag around the top (see diagram below). Loosely capped glass vials were left inside overnight to equilibrate. The vial caps were firmly closed before removing the plastic bag. Teflon tape was wrapped around the rim of each cap and the vials then tightly wrapped in a plastic bag.



Three days elapsed before the vials could be analyzed. The results obtained, using a Porapak Q column at 50^0 C and an electron-capture detector indicated no oxygen deficit in plots given 20% cuttings and carbon granules.

Samples obtained from:	Oxygen peak area / 10^5
Laboratory air	24.5, 23.4
N_2-purged flask	1.0, 1.0
O_2-purged flask	38.2
Control plot (north section)	23.2, 21.4
Manure mulch + 20% Invert	20.2, 23.3
Alta Ethylene C granules + 20%	24.4, 23.2

As I told you on the telephone today (June 6) I have installed xanthate integrating thermometers (should we call these *ZITS*, do you think?) on the carbon granule + 30% (unfert.) and on the plain 30% (unfert.) plots to test your theory about soil temperature being a factor determining growth.

I took soil samples from all plots given 20% invert. We will extract the oil from these using the Dean/Stark toluene Soxhlet method, keeping the oil in case anyone wants to do more target compound work (please let me know). I intend to sample this middle rate only this year except in the fall when perhaps we should do some plots at the low and high rate also, to get the range of oil concentrations at all three rates. Results of the June 1 sampling will follow.

Yours truly,

J.A.

cc. R. Scroggins

ETL Enviro-Test Laboratories
A Division of ETL Chemspec Analytical Limited

9936 - 67th Avenue — Edmonton, Alberta T6E 0P5 Telephone: (403) 434-9509 FAX: (403) 437-2311

ANALYSIS OF DRIED PLANT TISSUE AND SAMPLE EXTRACTS FOR TARGET POLYCYCLIC AROMATIC HYDROCARBONS

Submitted To:

Norwest Laboratories
9938 - 67 Avenue
Edmonton, Alberta
T6E 0P5

DATE: March 1, 1989
REF.#: 1510.REP

APPROVED BY _____
Doug Johnson, Residue Analyst

CERTIFIED BY _____
Gordon Nelson, Project Manager

ACCREDITED BY THE: AMERICAN INDUSTRIAL HYGIENE ASSOCIATION (AIHA) - Industrial Hygiene analysis
STANDARDS COUNCIL OF CANADA - Organic & Industrial Hygiene analysis

ETL

OVERVIEW

Three dried plant tissue samples and seven sample extracts were submitted to Enviro-Test Laboratories on December 14, 1988, for target polycyclic aromatic hydrocarbon (PAH) analysis. The target compounds chosen were a result of previous gas chromatography/mass spectrometry (GC/MS) characterization of diesel invert mud residue soil samples.

The compounds chosen represent a cross-section of boiling range and molecular weight (MW) of the PAH compounds previously isolated.

Each sample was spiked with deuterated PAH surrogate compounds to test efficiencies and the precision of the method.

The plant samples were extracted with acetone using a polytron to effect proper sample to solvent mixing. Then a partition extraction was performed to isolate the PAH's into dichloromethane (DCM). The organic solvent, DCM, was reduced to a small final volume, then a portion of this extract was cleaned up on alumina. During clean-up, an aromatic fraction was generated, which was screened on a gas chromatograph/flame ionization detector (GC/FID). The aromatic fraction then went to GC/MS for target compound analysis.

The residue samples were cleaned up on alumina as above, no prior extraction was required. Again, an aromatic fraction was generated, screened by GC/FID then injected on GC/MS for target compound analysis.

Extracted ion techniques were used for each sample to determine final concentrations using an Internal standard calculation method.

List of samples submitted:

LAB SAMPLE #	SAMPLE I.D
12-88-1510-1	21846 1/4 (Plant)
12-88-1510-2	21846 1/7 (Plant)
12-88-1510-3	21846 1/11 (Plant)
12-88-1510-4	22485-17 (Ext.)
12-88-1510-5	22485-18 (Ext.)
12-88-1510-6	22485-19 (Ext.)
12-88-1510-7	22485-20 (Ext.)
12-88-1510-8	Oct.19 Plot 10B (Subsoil Ext.)
12-88-1510-9	Oct.19 Plot 22A (Subsoil Ext.)
12-88-1510-10	Oct.19 Plot 24A (Subsoil Ext.)

METHOD OF EXTRACTION: PLANT

The plant samples were received dried and ground. A 10g portion was weighed into a centrifuge cup, then the deuterated surrogates were added. 130mL of acetone was added to the sample, then it was homogenized using a polytron for 3 minutes at medium speed. The resulting mixture was centrifuged to pack the plant tissue down, then the acetone was decanted into a 1L separatory funnel containing 300mL of deionized water. After adding 30g of NaCl to aid in separation, the water/acetone mixture was extracted with 60mL of dichloromethane (DCM). The extraction was repeated twice more, then the three extracts were combined in a round bottom flask after being dried through anhydrous sodium sulfate. This combined extract was reduced to a 1mL volume in DCM, then half of it was exchanged into hexane. The hexane portion was adsorbed onto a 3g portion of 1% deactivated neutral alumina. The 3g portion was dry packed onto a further 6g portion of the same alumina, then 3 fractions were generated, the first using 20mL of pentane to elute the aliphatics, the second using 50mL of benzene to elute the aromatics, and the third using 100mL of chloroform as a final wash on the column. The first fraction is generated as a clean-up, the second contains the PAH's, and the third is performed as a final wash to be sure all aromatics

were eluted from the column. (Not analyzed unless a problem arises with surrogates).

Fractions 1 and 2 were reduced to a 2mL final volume, then screened by GC/FID to determine suitable dilutions for GC/MS analysis. All of the fraction 2's were then analyzed by GC/MS. The following target compound list (Table 1) was chosen and analysis for these compounds was completed using anthracene D_{10} as internal standard.

RESIDUE:

100μL aliquots of the residue samples were adsorbed onto 3g portions of 1% deactivated neutral alumina, along with the same deuterated surrogate as for the plant samples. This 3g portion was dry packed onto a further 6g portion of the same alumina, and three fractions were generated, as above. Fractions 1 and 2 were reduced to a 2mL volume and screened by GC/FID, then fraction 2 was analyzed for the same target compounds, using GC/MS.

TABLE 1

TARGET PAH's	MOLECULAR wt.	METHOD OF QUANTITATION
1. Naphthalene	128	Naphthalene as standard
2. C_1 Naphthalenes	142	Naphthalene as standard
3. C_2 Naphthalenes	156	Naphthalene as standard
4. C_3 Naphthalenes	170	Naphthalene as standard
5. Biphenyl	154	Naphthalene as standard
6. Fluorene	166	Fluorene as standard
7. C_1 Fluorene	180	Fluorene as standard
8. Phenanthrene	178	Phenanthrene as standard
9. C_1 Dibenzothiophene	198	Phenanthrene as standard

Figure 1 shows a typical extracted ion current profile (EICP) for the target PAH's in one of the residues. This technique was used for each sample. Integrated area counts are generated by the GC/MS system and quantitation is completed using an internal standard calculation using anthracene - d_{10}.

Figure 2 is the total ion chromatogram of this sample which represents all the PAH compounds extracted from the sample.

QUALITY CONTROL:

Each sample was spiked with deuterated surrogates to determine extraction efficiency and precision. Table 2 is a summary of the spiked surrogate results. Due to a lack of certain surrogate compounds during the analytical phase, dibenzothiophene d_8 and chrysene d_{12} were quantitated against the internal standard.

TABLE 2

RECOVERY OF SURROGATE COMPOUNDS

	RANGE OF RECOVERIES		AVERAGE RECOVERY	
	PLANT	RESIDUE	PLANT	RESIDUE
1. Naphthalene - d_8	57%-61%	69%-86%	58%	77%
2. 2-Fluorobiphenyl	74%-96%	88%-122%	89%	108%
3. Biphenyl -d_{10}	54%-84%	79%-106%	72%	96%
4. Dibenzothiophene - d_8	65%-75%	73%-90%	71%	82%
5. Chrysene - d_{12}	36%-61%	60%-99%	52%	77%

	RELATIVE STANDARD DEVIATION	
	PLANT	RESIDUE
1. Naphthalene - d_8	4.5%	10.2%
2. 2-Fluorobiphenyl	11.4%	10.1%
3. Biphenyl -d_{10}	17.7%	10.5%
4. Dibenzothiophene - d_8	6.6%	7.6%
5. Chrysene - d_{12}	22.1%	18.2%

A method blank was completed for both the plants and the residues, and was analyzed for the target PAH compounds.

RESULTS:

Table 3 contains the results of the target PAH compounds for all samples. Results are on a dry weight basis for the plants, and are reported in ppm (μg/g). The detection limit set for plant sample analysis is 0.10ppm for all target PAH's, more sensitivity could be obtained if selected ion acquisition of data was performed.

Results for the residues are based on analysis of a known mass of residue, and the detection limit is set at 5.0ppm for all target PAH's.

Table 4 contains the results of the GC/FID screen of fraction 1. These results are presented as total extractable hydrocarbons, no hydrocarbon patterns were available. A calibrated mixture of C_{15} to C_{29} hydrocarbons was used to quantitate against.

TABLE 3

PAH's IN PLANT AND RESIDUES µg/g(ppm)

SAMPLE I.D.	Naph	C_1-Naph	C_2-Naph	C_3-Naph	Biph	Fluo	C_1-Fluo	Phen	C_1-Diben
21846 1/4 Plant 12-88-1510-1	N.D.	N.D.	N.D.	N.D.	N.D.	0.8	1.0	0.63	N.D.
21846 1/7 Plant 12-88-1510-2	N.D.	N.D.	N.D.	N.D.	N.D.	0.24	0.44	0.11	N.D.
21846 1/11 Plant 12-88-1510-3	N.D.	N.D.	N.D.	N.D.	N.D.	0.30	0.56	0.15	N.D.
22485-17 Ext. 12-88-1510-4	N.D.	30	72	33	23	N.D.	N.D.	36	N.D.
22485-18 Ext. 12-88-1510-5	N.D.	51	86	N.D.	20	130	68	38	5.0
22485-19 Ext. 12-88-1510-6	N.D.	N.D.	N.D.	N.D.	N.D.	65	17	43	19
22485-20 Ext. 12-88-1510-7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	38	34	22
Plot 10B Subs.Ext. 12-88-1510-8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	24	N.D.
Plot 22A Subs.Ext. 12-88-1510-9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	23	14	6.3
Plot 24A Subs.Ext. 12-88-1510-10	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	63	N.D.

Naph	= Naphthalene	Fluo	= Fluorene
C_1-Naph	= C_1 Naphthalenes	C_1 Fluo	= C_1 Fluorene
C_2-Naph	= C_2 Naphthalenes	Phen	= Phenanthrene
C_3-Naph	= C_3 Naphthalenes	C_1-Diben	= C_1-Dibenzothiophene
Biph	= Biphenyl	N.D.	= Not detected, less than 5.0ppm residue 0.10ppm plants

TABLE 4

TOTAL EXTRACTABLE ALIPHATIC HYDROCARBONS

LAB SAMPLE #	SAMPLE I.D.	TOTAL EXTRACTABLE HYDROCARBONS (Fr.1) ppm(µg/g)
12-88-1510-1	21846 1/4 Plant	66ppm
12-88-1510-2	21846 1/7 Plant	32ppm
12-88-1510-3	21846 1/11 Plant	54ppm
12-88-1510-4	22485-17 Ext.	208,000ppm
12-88-1510-5	22485-18 Ext.	406,000ppm
12-88-1510-6	22485-19 Ext.	412,000ppm
12-88-1510-7	22485-20 Ext.	253,000ppm
12-88-1510-8	Plot 10B Subs.Ext.	12,000ppm
12-88-1510-9	Plot 22A Subs.Ext.	16,000ppm
12-88-1510-10	Plot 24A Subs.Ext.	4600ppm

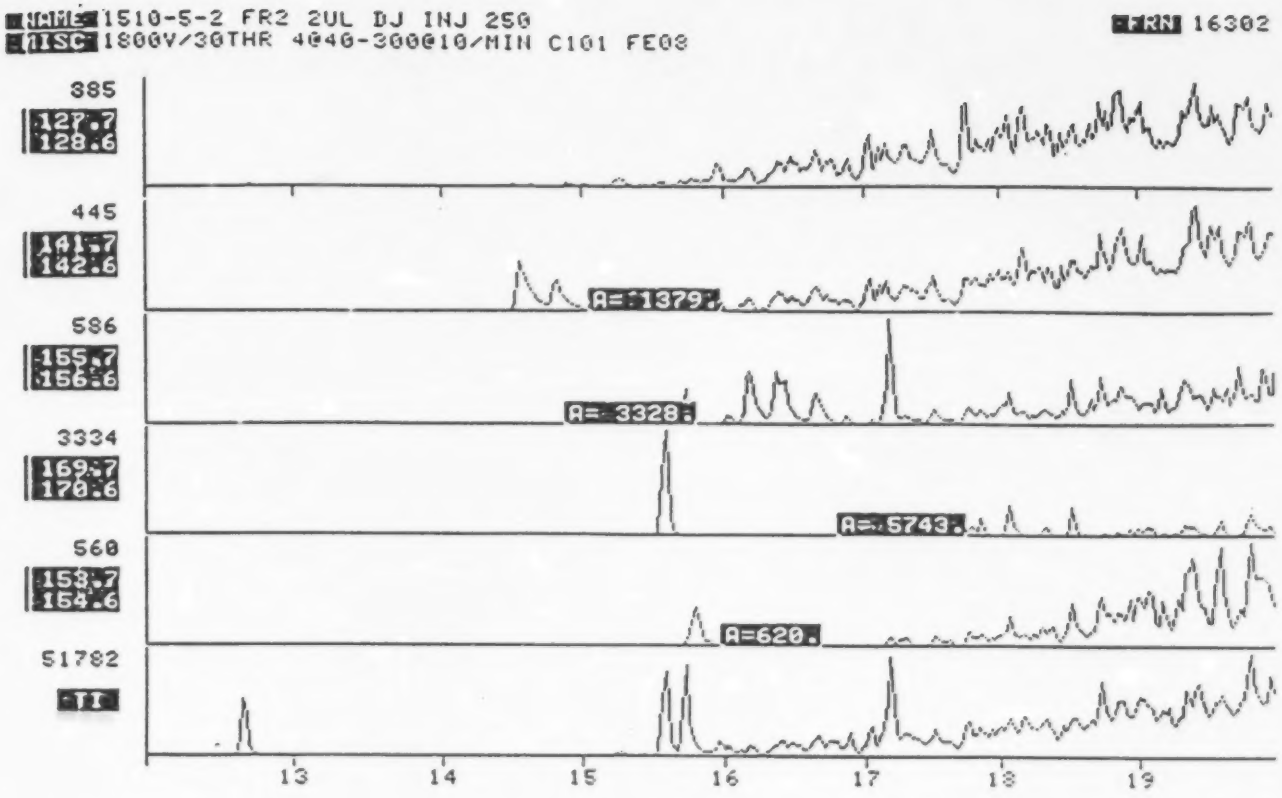
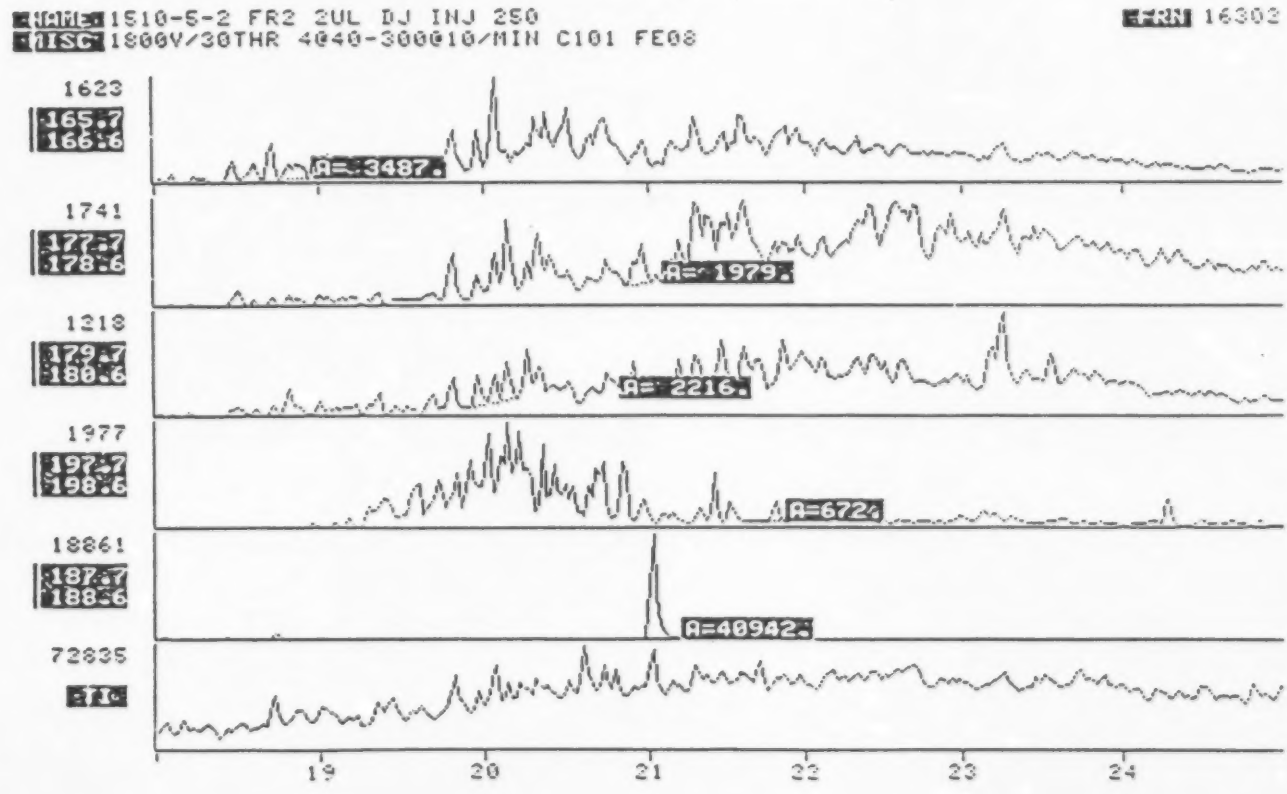


FIGURE 1: EXTRACTED ION CHROMATOGRAMS FOR SAMPLE 1510-5 Fr.2



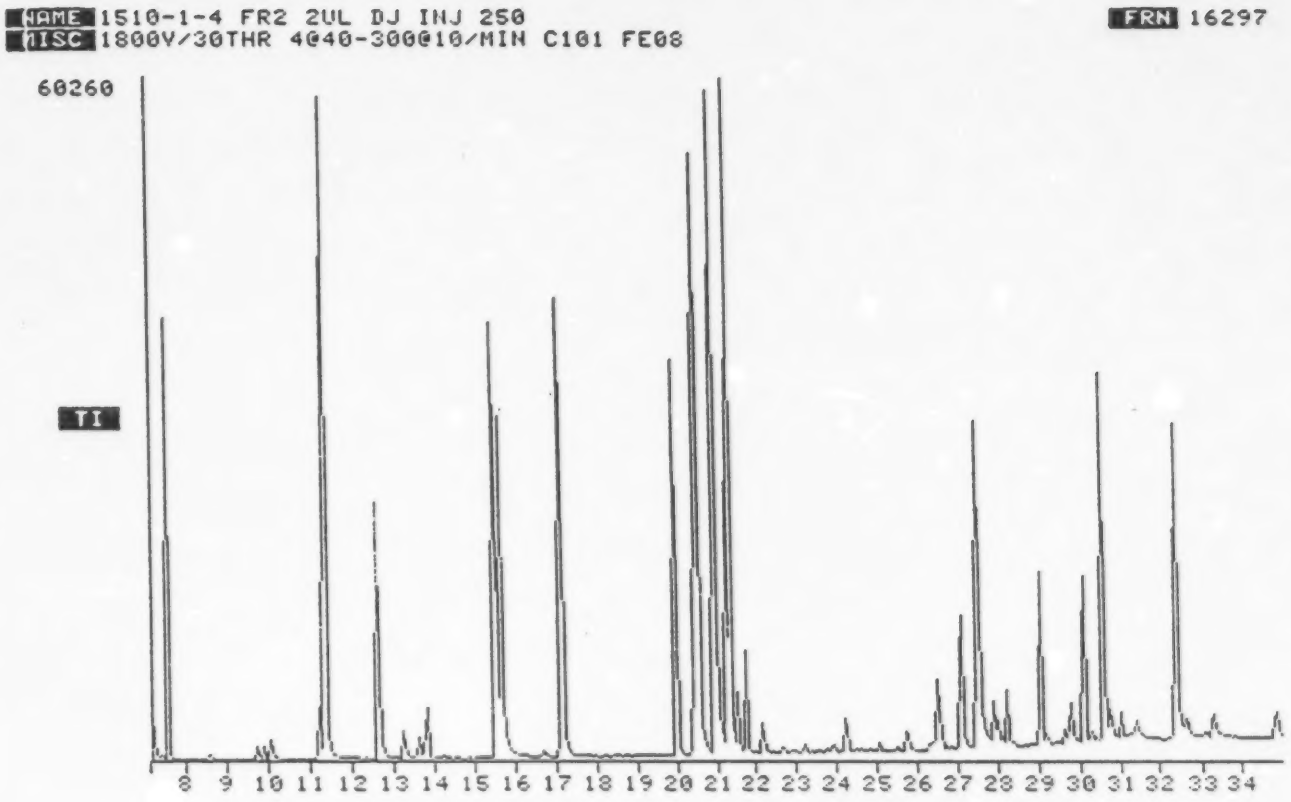


FIGURE 2: TIC OF SAMPLE 1510-1 Fr. 2 (PLANT)

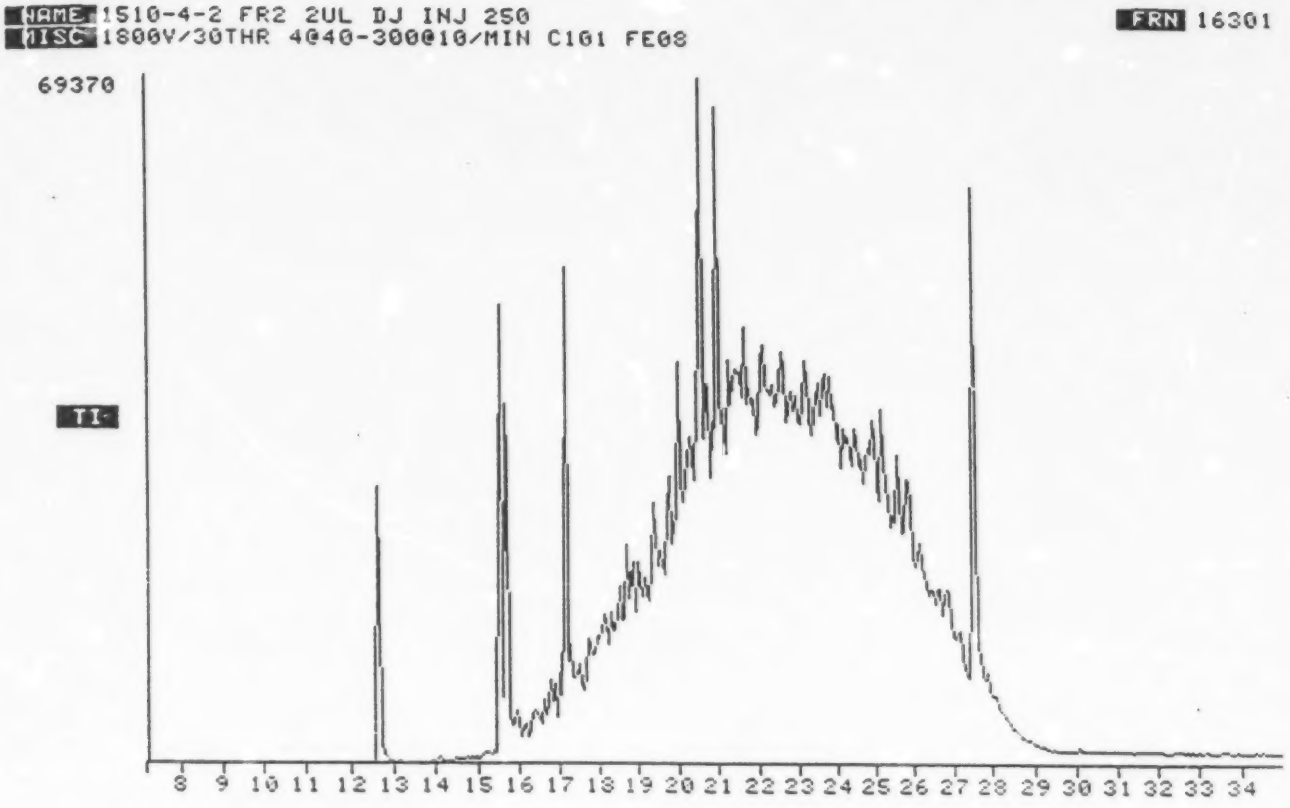


FIGURE 3: TIC OF SAMPLE 1510-4 (SOIL EXT.) Fr.2

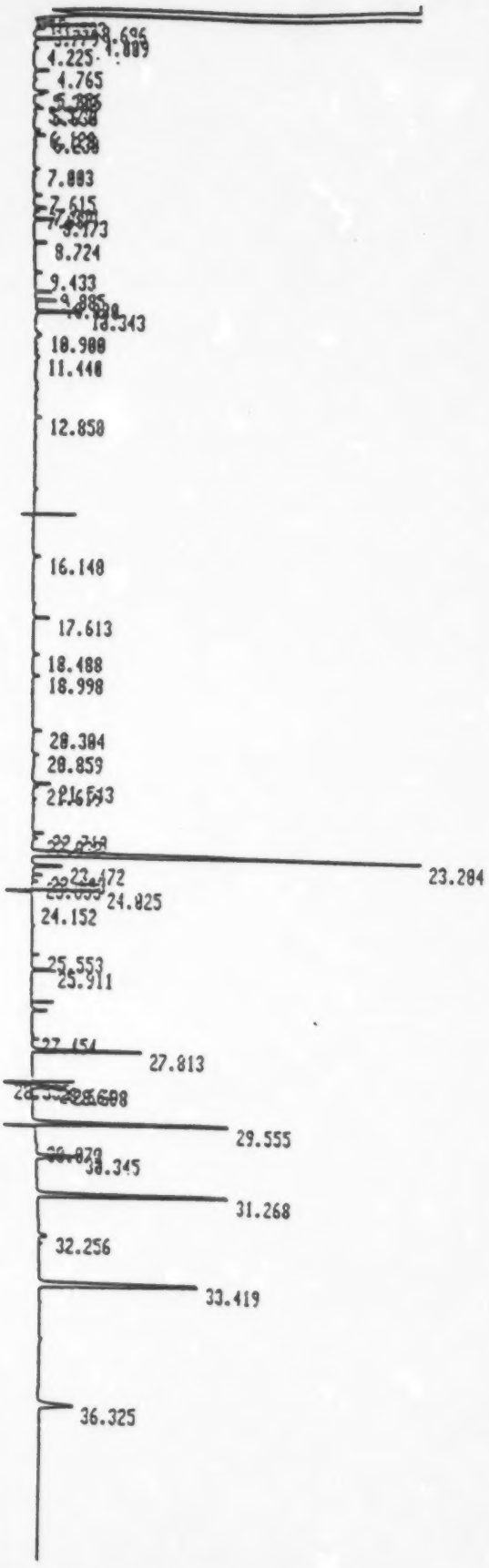
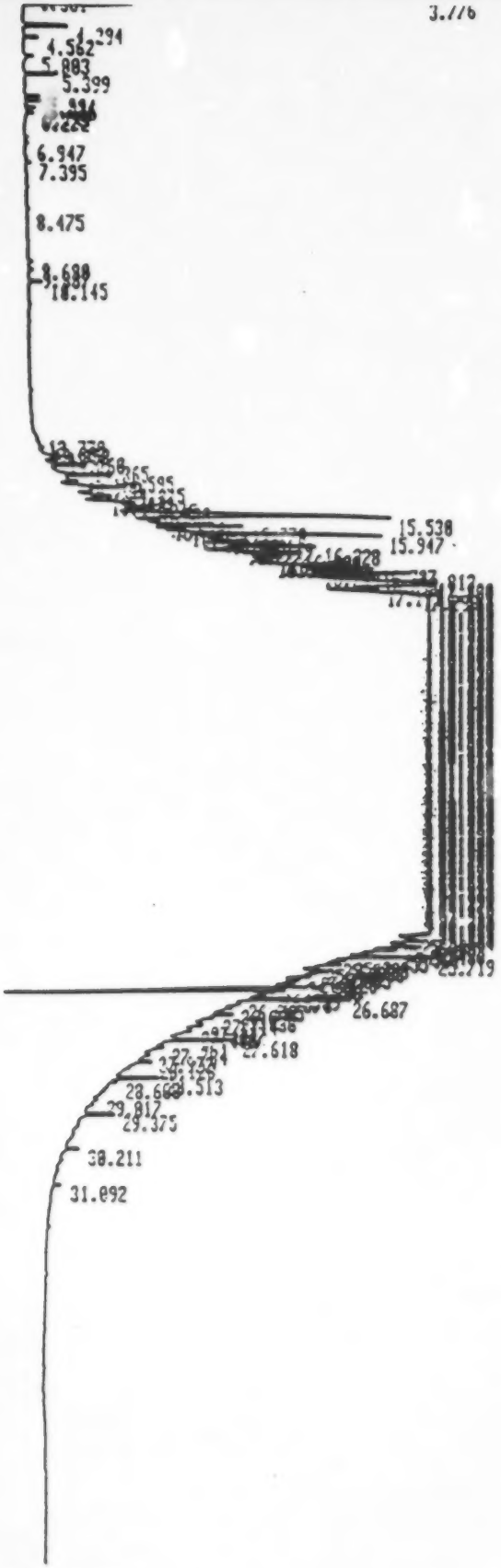


FIGURE 4: GC/FID CHROMATOGRAM OF SAMPLE 1510-1 Fr.1

FRACTION 5: GC/FID CHROMATOGRAM OF
SAMPLE 1510-4 Fr.1



TIMETABLE STOP

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